State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

APPENDICES

FOR THE

Report for the Air Monitoring
of Endosulfan
In Fresno County (Ambient) and in
San Joaquin County (Application)

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. C96-034

Date: April 17, 1998

Cal/EPA
California Environmental Protection Agency

Air Resources Board
P.O. Box 2815
2020 L Street
Sacramento, CA
95812-2815

MEMORANDUM

TO: Dr. John Sanders, Chief
Environmental Monitoring and Pest Management Branch
Department of Pesticide Regulations

FROM: George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division

DATE: August 1, 1996

SUBJECT: FINAL ENDOSULFAN MONITORING PROTOCOL

Attached is the final monitoring protocol, "Protocol for the Ambient Monitoring of Endosulfan in Fresno County During Summer, 1996." The protocol also includes the draft "Standard Operating Procedures for the Analysis of Endosulfan in the Ambient Air." Application monitoring for endosulfan will be conducted in Lake County in September.

If you or your staff have questions or need further information, please contact me at 263-1630 or Kevin Mongar at 263-2063.

Attachment

cc: Genevieve Shiroma, SSD (w/attachment)
Jeff Cook, MLD (w/attachment)
Bill Oslund, MLD (w/attachment)

APPENDIX I

SAMPLING PROTOCOL

State of California
California Environmental Protection Agency
AIR RESOURCES BOARD

Protocol for the Ambient Air Monitoring of Endosulfan In Fresno County During Summer, 1996

Engineering and Laboratory Branch

Monitoring and Laboratory Division

Project No. C96-034

Date: August 1, 1996

APPROVED:

David F Todd for
Kevin Mongar, Project Engineer

David F Todd for
Cynthia L. Castronovo, Manager
Testing Section

George Lew
George Lew, Chief
Engineering and Laboratory Branch

This protocol has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Protocol for the Ambient Air Monitoring
of Endosulfan
In Fresno County During Summer 1996

I. Introduction

At the request of the California Department of Pesticide Regulation (DPR), (March 20, 1996 Memorandum from John Sanders to George Lew) the Air Resources Board (ARB) staff will determine airborne concentrations of the pesticide endosulfan over a five week ambient monitoring program in populated areas. This monitoring will be done to fulfill the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions .... of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The monitoring is in support of the DPR toxic air contaminant program and will be conducted in Fresno County.

The method development results and Standard Operating Procedures for endosulfan analysis are included in this protocol as Attachment A.

II. Chemical Properties of Endosulfan

To fulfill the requirements of AB 1807/3219 (California Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), the Department of Pesticide Regulation has previously requested that the Air Resources Board document the airborne concentrations of the pesticide endosulfan [(3α,5aβ,6α,9α,9aβ)- or (3α,5aα,6β,9β,9aα)- 6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide].

The technical grades of endosulfan are mixtures of two stereoisomers α-Endosulfan (64-67%) and β-endosulfan (32-29%) with approximately 4% other material. α-Endosulfan [(3α,5aβ,6α,9α,9aβ)-6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide] (CAS:959-98-8) and β-endosulfan [3α,5aα,6β,9β,9aα)-6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide] (CAS: 33213-65-9) are colorless to brown crystals emitting a sulfur dioxide-like odor. Endosulfan has a molecular formula of $C_9H_6Cl_6O_3S$, a formula weight of 460.92 g/mole and a specific density of 1.745 at 20°C. Endosulfan has a vapor pressure of 10^{-5} mmHg at 25°C, but water solubility (S_w), and Henry's Constant (K_H) vary with isomer. α-Endosulfan S_w = 530 ppb at 25°C, $K_H = 1.01 \times 10^{-4}$ atm·m^3/mol at 25°C, β-endosulfan S_w = 280 ppb at 25°C, $K_H = 1.91 \times 10^{-5}$ atm·m^3/mol at 25°C. Both isomers are soluble in most organic solvents.

The hydrolysis half-life ($t_{1/2}$) of endosulfan in water (25°C and pH7) is 218 hours for α-endosulfan and 187 hours for β-endosulfan. In plants the $t_{1/2}$ for conversion of α-endosulfan to β-endosulfan is approximately 60 days, and the $t_{1/2}$ for the conversion of β-endosulfan to endosulfan sulfate is 800 days. Each isomer forms its respective sulfate on exposure to light in surface waters.

Degradation of endosulfan in soil yields a mixture of endosulfandiol, endosulfanhydroxy ether, endosulfan lactone and endosulfan sulfate. Endosulfan sulfate is the major biodegradation product in soils under aerobic, anaerobic and flooded conditions. In flooded soils, endosulfandiol and endohydroxy ether were also reported. In sandy loam soil, microorganisms are responsible for degrading endosulfan to endosulfandiol, and further to endosulfan α-hydroxy ether and trace amounts of endosulfan ether. Both products are subsequently converted to endosulfan lactone. This soil transformation pathway is followed by both isomeric forms.

The acute oral LD_{50} of endosulfan for rats in 70 mg/kg (aqueous), and 110 mg/kg in oil. Acute LC_{50} (1-hour) for rats > 21mg/L air. Acute dermal LD_{50} is 500 mg/kg for rats and 369 mg/kg for rabbits. The LC_{50} (96 hour) irrespective of isomer are 0.3 μg/L for rainbow trout, and 3.0 μg/L for white sucker. Endosulfan has entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984) based on its potential reproductive and neurotoxicity adverse health effects.

As of March 8, 1995, there were 19 active registrations for products containing endosulfan. Eighteen are agricultural products and one is a home-garden product. Formulations of endosulfan include granulars, emulsifiable concentrates and wettable powders. Technical endosulfan is formulated as a dust. The Signal Words on agricultural endosulfan-containing products are "Danger: or "Danger/Poison", and "Warning" on the home garden (9.15% Active Ingredient) product.

III. Sampling

Samples will be collected by passing a measured volume of ambient air through XAD-2 resin. The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest or refrigerator until desorbed with 3 ml of isooctane. The flow rate will be accurately measured and the sampling system operated continuously with the exact operating interval noted. The resin tubes will be protected from direct sunlight and supported about 1.5 meters above the ground during the sampling period. At the end of each sampling period the tubes will be capped and placed in culture tubes with an identification label affixed. Any endosulfan present in the sampled ambient air will be captured by the XAD-2 adsorbent. Subsequent to sampling, the sample tubes will be transported on ice, as soon as reasonably possible to the ARB Monitoring and Laboratory Division, Testing Section laboratory for analysis. The samples will be stored in the refrigerator or analyzed immediately.

A sketch of the sampling apparatus is shown in Attachment B. Calibrated rotameters will be used to set and measure sample flow rates. Samplers will be leak checked prior to and after each sampling period with the sampling cartridges installed. Any change in the flow rates will be recorded in the field log book. The field log book will also be used to record start and stop times, sample identifications and any other significant data

Ambient Monitoring

The use patterns for endosulfan suggest that ambient monitoring should take place in Fresno County during a 30- to 45-day sampling period in the months of July and August.

Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be in cotton or grape growing areas but not immediately adjacent to fields being treated. Background samples should be collected in an area distant to endosulfan applications. Replicate (collocated) samples are needed for five dates at each sampling location. The date chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be the same dates at every site.

Four sampling sites plus an urban background site were selected by ARB personnel from the areas of Fresno County where cotton farming is predominant. Sites were selected for their proximity to the fields with considerations for both accessibility and security of the sampling equipment. The five sites were at the following locations: Cantua Creek School, Cantua Creek; Westside Elementary School, Five Points; San Joaquin Elementary School, San Joaquin; Tranquility High School, Tranquility; ARB Ambient Air Monitoring Station, Fresno (background). Addresses for the sites are listed in Table 1.

TABLE 1. Ambient Sampling Sites

Cantua Creek School 19288 W. Clarkson Ave. Cantua Crk., 93608	Ron Garcia, District Superintendent (209) 829-3331
Westside Elementary School 19191 Excelsior Ave., Five Points, CA 93624	Baldomero Hernandez, Principal (209) 884-2492
San Joaquin Elementary School 8535 S. 9th, San Joaquin, CA 93660	Carlos Navarrette, Principal (209) 693-4321
Tranquility High School 6052 Juanche, Tranquility, CA 93668 Mailing address: P.O. Box 457	John Crider, Principal (209) 698-7205
Air Resources Board, Ambient Air Monitoring Station 3425 N First, Suit 205B, Fresno, CA 93726-6819 (Background Site)	Steve Rider (916) 327-4919 Peter Ouchida (916) 322-3719

The samples will be collected by ARB personnel over a five week period from July 29 - August 30, 1996. 24-hour samples will be taken Monday through Friday (4 samples/week) at a flow rate of approximately 2 liters per minute.

IV. Analysis

The method development results and Standard Operating Procedure (SOP) for analysis of endosulfan are included in this protocol as Attachment A.

V. Quality Assurance

Field Quality Control for the ambient monitoring will include: 1) Five field spikes (same environmental and experimental conditions as those occurring at the time of ambient sampling) will be prepared by the Quality Management and Operations Support Branch (QMSOB) and spiked at five different levels. The field spikes will be obtained by sampling ambient air at the background monitoring site for 24 hour periods at 2 L/minute. 2) Five trip spikes will be prepared by the QMOSB and spiked at five different levels. 3) Replicate samples will be taken for five dates at each sampling location. 4) Trip blanks will be obtained at each of the five sampling locations. Procedures will follow ARB's "Quality Assurance Plan for Pesticide Monitoring" (Attachment C).

The instrument dependent parameters (reproducibility, linearity and minimum detection limit) will be checked prior to analysis. A chain of custody sheet will accompany all samples. Rotameters will be calibrated prior to and after sampling in the field.

VI. Personnel

ARB personnel will consist of Kevin Mongar (Project Engineer) and an Instrument Technician.

Attachment A

State of California
Air Resources Board
Monitoring and Laboratory Division/ELB

Standard Operating Procedure for the Analysis of Endosulfan in Ambient Air

1. SCOPE

This is a gas chromatography/electron capture method for the determination of endosulfan from ambient air samples. The method was adapted from J&W Scientific GC Chromatograms, Chlorinated pesticides, 1994-95 Catelogue, p120.

2. SUMMARY OF METHOD

The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest or refrigerator until desorbed with 3 ml of isooctane. The injection volume is 2 ul. A gas chromatograph with a DB-608 capillary column and an electron capture detector is used for analysis.

3. INTERFERENCES/LIMITATIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank must be done with each batch of samples to detect any possible method interferences.

It has been noted that when high concentrations of endosulfan are injected, often a significant amount remains in the needle and results in carry over to the next injection. For this reason all injections should be done at least in duplicate. If significant carry over is observed, the run should be repeated.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Varian 3400 gas chromatograph
Varian 604 Data System
Varian 8200 Autosampler

Detector: 350°C
Injector: 250°C
Column: J&W Scientific DB-608, 30 meter, 0.32 mm i.d., 0.5 um film thickness.

Program: Initial 80°C, hold 1 min, to 265°C @ 50°C/min., hold 25 min. Retention times: Endosulfan I = 13.8 min., Endosulfan II = 17.8 min., Endosulfan sulfate = 20.8 min. End of run = 29.7 min.

Splitter open @ 0.8 min., flow 50 mL/min.

Flows:
column: He, 1.7 mL/min, 8 psi
Make up = 30 mL/min. N_2

B. AUXILIARY APPARATUS:

1. Glass amber vials, 8 mL capacity.
2. Vial Shaker, SKC, or equiv.
3. Autosampler vials with septum caps.

C. REAGENTS

1. Isooctane, Pesticide Grade, or better
2. Endosulfan I and II (alpha and beta isomers), Endosulfan sulfate 98% pure or better (Chem Service).

5. ANALYSIS OF SAMPLES

1. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which results in possible carry-over contamination.

2. If a standard curve is not generated each day of analysis, at least one calibration sample must be analyzed for each batch of ten samples. The response of the standard must be within 10% of previous calibration analyses.

3. Carefully score the primary section end of the sampled XAD-2 tube above the retainer spring and break at the score. Remove the glass wool plug from the primary end of the XAD-2 tube with forceps and place it into an 8 mL amber colored sample vial. Pour the XAD-2 into the vial and add 3.0 mL isooctane. Retain the secondary section of the XAD-2 tube for later analysis to check the possibility of breakthrough.

4. Place the sample vial on a desorption shaker for 25 minutes. Remove the isooctane extract and store in a second vial at 4°C until analysis.

5. After calibration of the GC system, inject 2.0 ul of the extract. If the resultant peaks for endosulfan have a measured area greater than that of the highest standard injected, dilute the sample and re-inject.

6. Calculate the concentration in ng/mL based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.

7. The atmospheric concentration is calculated according to:

Conc., ng/m^3 = (Extract Conc., ng/mL X 3 mL) / Air Volume Sampled, m^3

6. QUALITY ASSURANCE

A. INSTRUMENT REPRODUCIBILITY

Six replicate injections of 2 uL each were made of a standard containing all three of the endosulfans in order to establish the reproducibility of this instrument. This data is shown in TABLE 1.

TABLE 1. INSTRUMENT REPRODUCIBILITY

AMOUNT INJECTED (ng/mL)	Endosulfan I	Endosulfan II	Endosulfan sulfate
1.0	17,953 ± 450 (±3%)	11,662 ±1494 (±13%)	15,235± 1,288 (±8%)
5.0	50,537 ± 739 (+2%)	37,134 ±779 (±2%)	38,742 ±2,429 (±6%)
25.0	383,214 ± 14,464(±4%)	329,052 ±17,357 (±6%)	300,835 ±21,662 (± 7%)
50.0	714,243 ± 4,330 (±1%)	616,688 ±9,200 (± 2%)	614,554 ±14,658 (±2%)

B. LINEARITY

A four point calibration curve was made ranging from 1.0 ng/mL to 50.0 ng/mL (from TABLE 1). The coresponding equations and correlation coefficients are:

Endosulfan I $y = 6.8599 \times 10^{-5} X + 0.2543$ Corr. = .998

Endosulfan II $y = 7.9079 \times 10^{-5} X + 0.8138$ Corr. = .999

Endosulfan sulfate $y = 8.0121 \times 10^{-5} X + 0.8334$ Corr. = .999

C. MINIMUM DETECTION LIMIT

Using the equations above and the data below, the minimum detection limit for Endosulfan was calculated by:

$$MDL = |i| + 3(s.d._{low})$$

where: $|i|$ = the absolute value of the intercept of the standard curve (from above).

$s.d._{low}$ = the standard deviation of the lowest concentration used for the standard curve.

For Endosulfan I: lowest concentration used = 1.0 $\pm$ 0.29 ng/mL

MDL = |0.2543| + 3(0.29) = 1.12 ng/mL

For Endosulfan II: lowest concentration used = 1.0 $\pm$ 0.93 ng/mL

MDL = |0.8138| + 3(0.93) = 3.6 ng/mL

For Endosulfan sulfate: lowest concentration used = 1.0 $\pm$ 0.94 ng/mL

MDL = |0.8334| +3(0.94) = 3.7 ng/mL

Based on the 3 mL extraction volume and assuming a sample volume of 2.7 m^3 (1.9 lpm for 24 hours):

Endosulfan I: $\frac{1.12\ ng/mL\ (3\ mL)}{2.7\ m^3}$ = 1.2 ng/m^3 per 24-hour sample

Endosulfan II: $\frac{3.6\ ng/mL\ (3\ mL)}{2.7 m^3}$ = 4.0 ng/m^3 per 24-hour sample

Endosulfan sulfate: $\frac{3.7\ ng/mL\ (3\ mL)}{2.7\ m^3}$ = 4.1 ng/m^3 per 24-hour sample

D. COLLECTION AND EXTRACTION EFFICIENCY (RECOVERY)

Collection and extraction efficiency data for Endosulfan on XAD-2 is presented in TABLE 2.

TABLE 2. COLLECTION AND EXTRACTION EFFICIENCY FOR ENDOSULFAN ON XAD-2

ENDOSULFAN I			ENDOSULFAN II			ENDOSULFAN SULFATE		
Amount Spiked (ng)	Amount Recovered (ng)	(%)	Amount Spiked (ng)	Amount Recovered (ng)	(%)	Amount Spiked (ng)	Amount Recovered (ng)	(%)
50.0	50.4	101 ± 1	50.0	40.5	81 ± 3	50.0	34.4	69 ± 4
150	134.3	90 ± 1	150	106.4	71 ± 1	150	9105	61 ± 2

The standards were spiked on the primary section of an XAD-2 tube. The tube was then subjected to an air flow of approximately 2 lpm for 24 hours. The tubes were run at an ambient temperature of approximately 85°F. The primary sections were then desorbed with 3.0 mL of isooctane and analyzed by capillary column GC/ECD.

E. STORAGE STABILITY

Storage stability studies were done in triplicate for 1.0 ng endosulfan spikes on XAD-2 tube primary sections over a period of 20 days. The percent recovery data for storage stability is presented in TABLE 3.

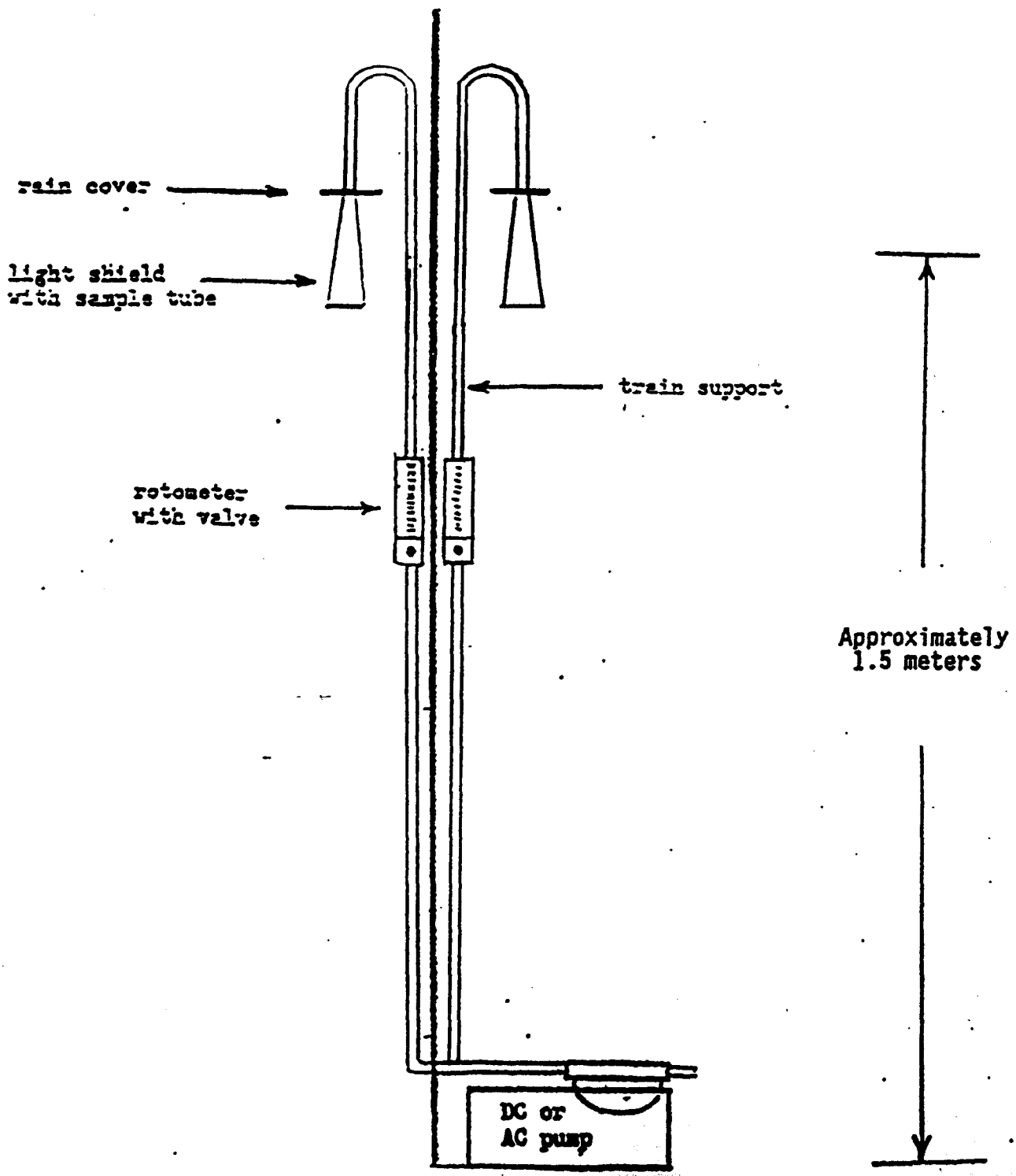
TABLE 3. ENDOSULFAN STORAGE STABILITY AT 4°C

50 ng each spiked	PERCENT RECOVERY			
	0 DAY	2 DAYS	7 DAYS	20 DAYS
Endosulfan I	95±2	102±1	105±2	103±1
Endosulfan II	84±5	81±1	87±3	89±3%
Endosulfan Sulfate	79±6	72±1	80±4	86±7%

F. BREAKTHROUGH

Triplicate tubes were spiked at 50, 100 and 500 ng/tube (Endosulfan I, Endosulfan II and Endosulfan sulfate) then run for 24 hours at approximately 2 lpm, prior to analysis. No endosulfan was detected in the secondary of any of the tubes.

Attachment B


rain cover
light shield
with sample tube
train support
rotometer
with valve
DC or
AC pump
Approximately
1.5 meters

Attachment C

State of California
California Environmental Protection Agency
Air Resources Board

QUALITY ASSURANCE PLAN

FOR PESTICIDE MONITORING

Prepared by the

Monitoring and Laboratory Division

and

Stationary Source Division

Revised: February 4, 1994

APPROVED:

Geraldine Shimmin, Chief
Toxic Air Contaminant
Identification Branch

_____, Chief
Quality Management and Operations
Support Branch

_____, Chief
Engineering Evaluation Branch

This Quality Assurance Plan has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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APPENDIX

QUALITY ASSURANCE PLAN FOR PESTICIDE MONITORING

I. Introduction

At the request of the Department of Pesticide Regulation (DPR), the Air Resources Board (ARB) documents the "level of airborne emissions" of specified pesticides. This is usually accomplished through two types of monitoring. The first consists of one month of ambient monitoring in the area of, and during the season of, peak use of the specified pesticide. The second is monitoring near a field during and after (up to 72 hours) an application has occurred. These are referred to as ambient and application monitoring, respectively. To help clarify the differences between these two monitoring programs, ambient and application are highlighted in bold in this document when the information applies specifically to either program. The purpose of this document is to specify quality assurance activities for the sampling and laboratory analysis of the monitored pesticide.

A. Quality Assurance Policy Statement

It is the policy of the ARB to provide DPR with as reliable and accurate data as possible. The goal of this document is to identify procedures that ensure the implementation of this policy.

B. Quality Assurance Objectives

Quality assurance objectives for pesticide monitoring are: (1) to establish the necessary quality control activities relating to site selection, sample collection, sampling protocol, sample analysis, data reduction and validation, and final reports; and (2) to assess data quality in terms of precision, accuracy and completeness.

II. Siting

Probe siting criteria for ambient pesticide monitoring are listed in TABLE 1. Normally four sites will be chosen. The monitoring objective for these sites is to measure population exposure near the perimeter of towns or in the area of the town where the highest concentrations are expected based on prevailing winds and proximity to applications. One of these sites is usually designated to be an urban area "background" site and is located away from any expected applications; however, because application sites are not known prior to the start of monitoring, a "zero level" background may not occur. Detectable levels of some pesticides may also be found at an urban area background site if they are marketed for residential as well as commercial use.

Probe siting criteria for placement of samplers near a pesticide application for collection of samples are the same as ambient monitoring (TABLE 1). In addition, the placement of the application samplers should be to obtain upwind and downwind concentrations of the pesticide. Since winds are variable and do not always conform to expected patterns, the goal is to surround the

application field with one sampler on each side (assuming the normal rectangular shape) at a distance of about 20 yards from the perimeter of the field. However, conditions at the site will dictate the actual placement of monitoring stations. Once monitoring has begun, the sampling stations will not be moved, even if the wind direction has changed.

III. Sampling

All sampling will be coordinated through the County Agricultural Commissioner's Office and the local Air Quality Management District (AQMD) or Air Pollution Control District (APCD). Monitoring sites will be arranged through the cooperation of applicators, growers or owners for application monitoring. For selection of ambient sites, ARB staff will work through authorized representatives of private companies or government agencies.

A. Background Sampling

A background sample will be taken at all sites prior to an application. It should be a minimum of one hour and longer if scheduling permits. This sample will establish if any of the pesticide being monitored is present prior to the application. It also can indicate if other environmental factors are interfering with the detection of the pesticide of concern during analysis.

While one of the sampling sites for ambient monitoring is referred to as an "urban area background," it is not a background sample in the conventional sense because the intent is not to find a non-detectable level or a "background" level prior to a particular event (or application). This site is chosen to represent a low probability of finding the pesticide and a high probability of public exposure if significant levels of the pesticide are detected at this urban background site.

B. Schedule

Samples for ambient pesticide monitoring will be collected over 24-hour periods on a schedule, in general, of 4 samples per week for 4 weeks. Field application monitoring will follow the schedule guidelines outlined in TABLE 2.

C. Blanks and Spikes

Field blanks should be included with each batch of samples submitted for analysis. This will usually require one blank for an application monitoring and one blank per week for an ambient monitoring program. Whenever possible, trip spikes should be provided for both ambient and application monitoring. The spiked samples should be stored in the same manner as the samples and returned to the laboratory for analysis.

D. Meteorological Station

Data on wind speed and direction will be collected during application monitoring by use of an on-site meteorological station. If appropriate

equipment is available, temperature and humidity data should also be collected and all meteorological data recorded on a data logger. Meteorological data are not collected for ambient monitoring.

E. Collocation

For both ambient and application monitoring, precision will be demonstrated by collecting samples from a collocated sampling site. An additional ambient sampler will be collocated with one of the samplers and will be rotated among the sampling sites so that duplicate samples are collected at at least three different sites. The samplers should be located between two and four meters apart if they are high volume samplers in order to preclude airflow interference. This consideration is not necessary for low (<20 liters/min.) flow samplers. The duplicate sampler for application monitoring should be downwind at the sampling site where the highest concentrations are expected. When feasible, duplicate application samples should be collected at every site.

F. Calibration

Field flow calibrators (rotometers, flow meters or critical orifices) shall be calibrated against a referenced standard prior to a monitoring period. This referenced standard should be verified, certified or calibrated with respect to a primary standard at least once a year with the method clearly documented. Sampling flow rates should be checked in the field and noted before and after each sampling period. Before flow rates are checked, the sampling system should be leak checked.

G. Flow Audit

A flow audit of the field air samplers should be conducted by an independent agency prior to monitoring. If results of this audit indicate actual flow rates differ from the calibrated values by more than 10%, the field calibrators should be rechecked until they meet this objective.

H. Log Sheets

Field data sheets will be used to record sampling date and location, initials of individuals conducting sampling, sample number or identification, initial and final time, initial and final flow rate, malfunctions, leak checks, weather conditions (e.g., rain) and any other pertinent data which could influence sample results.

I. Preventative Maintenance

To prevent loss of data, spare pumps and other sampling materials should be kept available in the field by the operator. A periodic check of sampling pumps, meteorological instruments, extension cords, etc., should be made by sampling personnel.

TABLE 1. PESTICIDE PROBE SITING CRITERIA SUMMARY

The following probe siting criteria apply to pesticide monitoring and are summarized from the U.S. EPA ambient monitoring criteria (40 CFR 58) which are used by the ARB.

Height Above Ground (Meters)	Minimum Distance From Supporting Structure (Meters)		Other Spacing Criteria
	Vertical	Horizontal	
2-15	1	1	1. Should be 20 meters from trees. 2. Distance from sampler to obstacle, such as buildings, must be at least twice the height the obstacle protrudes above the sampler. 3. Must have unrestricted air-flow 270° around sampler. 4. Samplers at a collocated site (duplicate for quality assurance) should be 2-4 meters apart if samplers are high flow, >20 liters per minute.

TABLE 2. GUIDELINES FOR APPLICATION SAMPLING SCHEDULE

All samplers should be sited approximately 20 yards from the edge of the field; four samplers to surround the field whenever possible. At least one site should have a collocated (duplicate) sampler.

The approximate sampling schedule for each station is listed below; however, these are only approximate guidelines since starting time and length of application will dictate variances.

- Background sample (minimum 1-hour sample: within 24 hours prior to application).
- Application + 1 hour after application combined sample.
- 2-hour sample from 1 to 3 hours after the application.
- 4-hour sample from 3 to 7 hours after the application.
- 8-hour sample from 7 to 15 hours after the application.
- 9-hour sample from 15 to 24 hours after the application.
- 1st 24-hour sample starting at the end of the 9-hour sample.
- 2nd 24-hour sample starting 24 hours after the end of the 9-hour sample.

IV. Protocol

Prior to conducting any pesticide monitoring, a protocol, using this document as a guideline, will be written by the ARB staff. The protocol describes the overall monitoring program, the purpose of the monitoring and includes the following topics:

1. Identification of the sample site locations, if possible.

2. Description of the sampling train and a schematic showing the component parts and their relationship to one another in the assembled train, including specifics of the sampling media (e.g., resin type and volume, filter composition, pore size and diameter, catalog number, etc.).

3. Specification of sampling periods and flow rates.

4. Description of the analytical method.

5. Tentative test schedule and expected test personnel.

Specific sampling methods and activities will also be described in the monitoring plan (protocol) for review by ARB and OPR. Criteria which apply to all sampling include: (1) chain of custody forms (APPENDIX I), accompanying all samples, (2) light and rain shields protecting samples during monitoring, and (3) storing samples in an ice chest (with dry ice if required for sample stability) or freezer, until delivery to the laboratory. The protocol should include: equipment specifications (when necessary), special sample handling and an outline of sampling procedures. The protocol should specify any procedures unique to a specific pesticide.

V. Analysis

Analysis of all field samples must be conducted by a fully competent laboratory. To ensure the capability of the laboratory, an analytical audit and systems audit should be performed by the ARB Quality Management and Operations Support Branch (QMOSB) prior to the first analysis. After a history of competence is demonstrated, an audit prior to each analysis is not necessary. However, during each analysis spiked samples should be provided to the laboratory to demonstrate accuracy.

A. Standard Operating Procedures

Analysis methods should be documented in a Standard Operating Procedure (S.O.P.) before monitoring begins. The S.O.P. includes: instrument and operating parameters, sample preparation, calibration procedures and quality assurance procedures. The limit of quantitation must be defined if different than the limit of detection. The method of calculating these values should also be clearly explained in the S.O.P.

1. Instrument and Operating Parameters

A complete description of the instrument and the conditions should be given so that any qualified person could duplicate the analysis.

2. Sample Preparation

Detailed information should be given for sample preparation including equipment and solvents required.

3. Calibration Procedures

The S.O.P. plan will specify calibration procedures including intervals for recalibration, calibration standards, environmental conditions for calibrations and a calibration record keeping system. When possible, National Institute of Standards and Technology traceable standards should be used for calibration of the analytical instruments in accordance with standard analytical procedures which include multiple calibration points that bracket the expected concentrations.

4. Quality Control

Validation testing should provide an assessment of accuracy, precision, interferences, method recovery, analysis of pertinent breakdown products and limits of detection (and quantitation if different from the limit of detection). Method documentation should include confirmation testing with another method when possible, and quality control activities necessary to routinely monitor data quality control such as use of control samples, control charts, use of surrogates to verify individual sample recovery, field blanks, lab blanks and duplicate analysis. All data should be properly recorded in a laboratory notebook.

The method should include the frequency of analysis for quality control samples. Analysis of quality control samples are recommended before each day of laboratory analysis and after every tenth sample. Control samples should be found to be within control limits previously established by the lab performing the analysis. If results are outside the control limits, the method should be reviewed, the instrument recalibrated and the control sample reanalyzed.

All quality control studies should be completed prior to sampling and include recovery data from at least three samples spiked at least two concentrations. Instrument variability should be assessed with three replicate injections of a single sample at each of the spiked concentrations. A stability study should be done with triplicate spiked samples being stored under actual conditions and analyzed at appropriate time intervals. This study should be conducted for a minimum period of time equal to the anticipated storage period. Prior to each sampling study, a conversion/collection efficiency study should be conducted under field conditions (drawing ambient air through spiked sample media at actual flow rates for the recommended sampling time) with three

replicates at two spiked concentrations and a blank. Breakthrough studies should also be conducted to determine the capacity of the adsorbent material if high levels of pesticide are expected or if the suitability of the adsorbent is uncertain.

VI. Final Reports and Data Reduction

The mass of pesticide found in each sample should be used along with the volume of air sampled (from the field data sheet) to calculate the mass per volume for each sample. For each sampling date and site, concentrations should be reported in a table as ug/m^3 (microgram per cubic meter). When the pesticide exists in the vapor phase under ambient conditions, the concentration should also be reported as ppbv (parts per billion, by volume) or the appropriate volume-to-volume units. Collocated samples should be reported separately as raw data, but then averaged and treated as a single sample for any data summaries. For samples where the end flow rate is different from that set at the start of the sampling period, the average of these two flow rates should be used to determine the total sample volume; however, the minimum and maximum concentrations possible for that sample should also be presented.

The final report should indicate the dates of sampling as well as the dates of analyses. These data can be compared with the stability studies to determine if degradation of the samples has occurred.

Final reports of all monitoring are sent to the Department of Pesticide Regulation, the Agricultural Commissioner's Office, the local AQMD as well as the applicator and/or the grower. Final reports are available to the public by contacting the ARB Engineering Evaluation Branch.

A. Ambient Reports

The final report for ambient monitoring should include a map of the monitored area which shows nearby towns or communities and their relationship to the monitoring stations, along with a list of the monitoring locations (e.g., name and address of the business or public building). A site description should be completed for any monitoring site which might have characteristics that could affect the monitoring results (e.g., obstructions). For ambient monitoring reports, information on terrain, obstructions and other physical properties which do not conform to the siting criteria or may influence the data should be described.

Ambient data should be summarized for each monitoring location by maximum and second maximum concentration, average (using only those values greater than the minimum quantitation limit), total number of samples and number of samples above the minimum quantitation limit. For this purpose, collocated samples are averaged and treated as a single sample.

B. Application Reports

Similarly, a map or sketch indicating the general location (nearby towns, highways, etc.) of the field chosen for application monitoring should be included as well as a detailed drawing of the field itself and the relative positions of the monitors. For application monitoring reports, as

much data as possible should be collected about the application conditions (e.g., formulation, application rate, acreage applied, length of application and method of application). This may be provided either through a copy of the Notice of Intent, the Pesticide Control Advisor's (PCA) recommendation or completion of the Application Site Checklist (APPENDIX II). Wind speed and direction data should be reported for the application site during the monitoring period. Any additional meteorological data collected should also be reported.

C. Quality Assurance

All quality control and quality assurance samples (blanks, spikes, etc.) analyzed by the laboratory must be reported. Results of all method development and/or validation studies (if not contained in the S.O.P.) will also be reported. The results of any quality assurance activities conducted by an agency other than the analytical laboratory should be included in the report as an appendix. This includes analytical audits, system audits and flow rate audits.

APPENDIX II

LABORATORY REPORT

Worker Health and Safety Laboratory

Center for Analytical Chemistry
3292 Meadowview Road
Sacramento, California
916-262-2079

Air Sample Analysis Report

for

Endosulfan Application

Submitted by:

Sheila Margetich
Supervisor
Worker Health and Safety Laboratory

9-29-97

Table of Contents

I. Summary of ARB/CAC Contract

The Worker Health and Safety Laboratory (WHS) of the Center for Analytical Chemistry (CAC) was contracted by the Air Resources Board to perform the analysis of air samples. In partial agreement of that contract, we analyzed one set of Endosulfan application samples plus accompanying QA.

The following Table 1 summarizes the 51 Endosulfan samples submitted by ARB and their analytical completion dates. Please see Attachment A1 ➢ A3 for the chain of custody forms that accompanied these samples. The analytical results are presented in Table 2. Analyses were performed for Endosulfan I, II and for Endosulfan Sulfate for each sample.

TABLE 1. ARB AIR SAMPLE LOG WITH ANALYTICAL COMPLETION DATES

Date Received	ARB Logbook Numbers (Inclusive)	Total # of air samples	Analytical Completion Date
4-7-97	Endosulfan Application 1-8	8	4-21-97
4-7-97	Endosulfan Application QA-TS spikes	4	4-21-97
4-11-97	Endosulfan Application 13-51	39	5-1-97

TABLE 2.
ANALYTICAL RESULT RECORD

ARB Endosulfan Application Logbook Number	ARB Field Sample Number	Endosulfan I * ug/sample	Endosulfan II ** ug/sample	Endosulfan Sulfate *** ug/sample	WHS Lab Number
1	ENDEB	ND	ND	ND	WHSC-83
3	ENDNB	ND	ND	ND	WHSC-84
5	ENDWB	ND	ND	ND	WHSC-85
7	ENDSB	ND	ND	ND	WHSC-86
13	ENDB-2	ND	ND	ND	WHSC-87
14	SB-2	ND	ND	ND	WHSC-88
15	WB-2	ND	ND	ND	WHSC-89
16	NB-2	ND	ND	ND	WHSC-90
17	ENDW-1	0.12	0.02	ND	WHSC-91
18	S-1	0.15	0.03	ND	WHSC-92
19	S-1D	0.21	0.04	ND	WHSC-93
20	E-1	0.22	0.03	ND	WHSC-94
21	N-1	0.21	0.03	ND	WHSC-95
22	ENDW-2	0.01	ND	ND	WHSC-96
23	S-2	0.10	ND	ND	WHSC-97
24	S-2D	0.12	ND	ND	WHSC-98
25	E-2	0.39	0.02	ND	WHSC-99
26	N-2	0.10	ND	ND	WHSC-100
27	ENDW-3	0.01	ND	ND	WHSC-101
28	S-3	0.55	0.02	ND	WHSC-102
29	S-3D	0.63	0.03	ND	WHSC-103
30	E-3	1.87	0.10	0.01	WHSC-104
31	N-3	0.35	0.02	ND	WHSC-105
32	ENDW-4	0.01	ND	ND	WHSC-106

* Endosulfan I Minimum Detection Limit: 0.003 ug/sample
** Endosulfan II Minimum Detection Limit: 0.006 ug/sample
*** Endosulfan Sulfate Minimum Detection Limit: 0.006 ug/sample

TABLE 2.
ANALYTICAL RESULT RECORD

ARB Endosulfan Application Logbook Number	ARB Field Sample Number	Endosulfan I * ug/sample	Endosulfan II ** ug/sample	Endosulfan Sulfate *** ug/sample	WHS Lab Number
33	S-4 •	0.10	0.01	ND	WHSC-107
34	S-4D •	0.14	0.01	ND	WHSC-108
35	E-4 •	1.17	0.07	0.01	WHSC-109
36	N-4 •	0.42	0.03	ND	WHSC-110
37	ENDW-5	ND	ND	ND	WHSC-111
38	S-5	0.07	ND	ND	WHSC-112
39	S-5D	0.08	ND	ND	WHSC-113
40	E-5	0.41	0.02	ND	WHSC-114
41	N-5	0.10	0.01	ND	WHSC-115
42	ENDW-6	0.05	ND	ND	WHSC-116
43	S-6	0.97	0.06	ND	WHSC-117
44	S-6D	1.38	0.14	0.01	WHSC-118
45	E-6	1.41	0.10	0.01	WHSC-119
46	N-6	0.23	0.02	ND	WHSC-120
47	ENDW-7	0.01	ND	ND	WHSC-121
48	S-7	0.83	0.10	0.01	WHSC-122
49	S-7D	0.88	0.12	0.01	WHSC-123
50	E-7	1.08	0.11	0.01	WHSC-124
51	N-7	0.18	ND	ND	WHSC-125

• These samples were labeled as "5s" instead of "4s", but we were able to separate the duplicate set of samples by their log IDs.

* Endosulfan I Minimum Detection Limit: 0.003 ug/sample

** Endosulfan II Minimum Detection Limit: 0.006 ug/sample

*** Endosulfan Sulfate Minimum Detection Limit: 0.006 ug/sample

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III. Summary of WHS Analytical Report

1. SCOPE:

This report covers the WHS analysis of samples labeled Endosulfan Application Log #1-51 (WHSC-83 through 125), and associated QA samples.

2. SUMMARY OF METHOD:

The analytical method titled "Standard Operating Procedure for the Analysis of Endosulfan in Ambient Air" as supplied by the State of California Air Resources Board was followed except for 1) the GC model, 2) the column, and 3) the column parameters. Please see Attachment B for the method SOP.

WHS Instrumentation

Hewlett Packard 5880A gas chromatograph and 7672 Autosampler

Column: J & W Scientific DB-17, 30 meter, 0.25 mm i.d., 0.5 um film thickness
Program: Initial 80 C, hold 1 min., to 260 C at 30 C/min., hold 20 min. Retention times:

Retention Times:	Endosulfan I	14.87 min.
	Endosulfan II	19.18 min.
	Endosulfan Sulfate	22.33 min.

Flows:
Column: He 20 psi
ECD make-up: 60 mL/min Ar/5% Methane

3. ANALYTICAL CALCULATIONS:

A. Theoretical calculation of MDL: The MDL was the quantity of each Endosulfan that gave a 5:1 S/N ratio. This corresponded to 0.002 ug Endosulfan I, and 0.004 ug Endosulfan II and Sulfate. Using a 2 uL injection volume, and 3 mL sample volume, this calculates to 0.003 ug/sample and 0.006 ug/sample, respectively.

B. Analytical verification of MDL: Please see Attachment C for chromatogram of a standard at the MDL concentration.

C. Sample result calculations: The 5880A data handling system, with a BASIC program to summarize and format the results, was used to compile the data. The multi-level calibration algorithm built into the system uses point-to-point lines to generate the calibration curve. The BASIC program also supplies the correct final volume to the built-in algorithm. According to the 5880 operating manual, the external.standard calculation is as follows:

Amount Y = (AREA)y * (RESPONSE)y * MULTIPLIER	
where	(AREA)y is the area or height of peak y (RESPONSE)y is the response factor (amount injected /area or height) of y MULTIPLIER is a constant specified during calibration

In our systems, the multiplier for standards is always 1 (equal to the ng injected), and for samples the total volume of extract is divided by the injection volume.

EXAMPLE:

$$\frac{78.76\ \text{H.U. sample}}{76.32\ \text{H.U. stand.}} \times \frac{0.05\ \text{ug stand.}}{\text{mL}} \times 2.0\ \text{uL stand. inj.} \times \frac{1.0\ \text{mL}}{1000\ \text{uL}} \times \frac{3.0\ \text{mL samp. FV}}{2.0\ \text{uL samp. inj.}} \times \frac{1000\ \text{uL}}{1.0\ \text{mL}} = 0.15\ \text{ug/sample}$$

Where:
H.U. = Height Units of peak

4. QUALITY ASSURANCE:

A. Instrument Linearity and Reproducibility: Replicate injections of 2 uL were made of standards containing all three of the Endosulfans in order to establish the reproducibility of the HP 5880A GC/ECD system. TABLE 3 lists the peak heights of these standards and the % variance of the multiple injections.

TABLE 3. INSTRUMENT LINEARITY AND REPRODUCIBILITY

Amount Injected	Peak Heights
0.004 ug each	
Endosulfan I	2.94-3.18 Avg 3.06 +/- 4%
Endosulfan II	1.85-1.96 Avg 1.91 +/- 3%
Endosulfan Sulfate	1.40-1.68 Avg 1.54 +/- 8%
0.010 ug each	
Endosulfan I	6.30-6.90 Avg 6.60 +/- 4%
Endosulfan II	3.86-4.20 Avg 3.22 +/- 4%
Endosulfan Sulfate	3.05-3.39 Avg 3.22 +/- 5%
0.050 ug each	
Endosulfan I	28.99-31.22 Avg 30.11 +/- 4%
Endosulfan II	17.78-19.50 Avg 18.65 +/- 4%
Endosulfan Sulfate	15.88-14.70 Avg 15.29 +/- 4%
0.100 ug each	
Endosulfan I	55.74-57.81 Avg 56.78 +/- 2%
Endosulfan II	34.36-35.86 Avg 35.11 +/- 2%
Endosulfan Sulfate	27.88-29.18 Avg 28.53 +/- 2%

4. QUALITY ASSURANCE: (cont.)

B. Standard Curve Linearity and r-value: A four point calibration curve was made ranging from 0.004 ug (Endosulfan I, II, and Sulfate) to 0.10 ug (Endosulfan I, II, and Sulfate). Please see Attachment D for a graph of the plotted r-value. Please see Attachment E1 ➢ E4 for chromatograms of the four standards comprising the standard curve.

The following table lists the r-values for the standard curves generated during the course of analyzing the Endosulfan samples.

TABLE 4. STANDARD CURVE "r" VALUES DURING COURSE OF THE PROJECT

Correlation Coefficients

Date	Endosulfan I	Endosulfan II	Endosulfan Sulfate
4-28-97	.9998	.9998	.9991
4-28-97	.9994	.9998	.9994
4-28-97	.9997	.9998	.9996
4-28-97	.9999	.9998	.9991
4-28-97	.9999	.9992	.9994
5-1-97	.9998	.9991	.9984
5-1-97	.9985	.9988	.9984
5-1-97	.9998	.9998	.9999
5-1-97	.9996	.9985	.9997
5-2-97	.9997	.9992	.9987

C. Analytical result acceptance criteria: Analytical acceptance criteria based on the linearity and reproducibility of standard curves are detailed in Attachment F, our SOP numbered WHS-AD-11 and titled "Data Generation and Reporting".

4. QUALITY ASSURANCE: (cont.)

D. Quality Assurance Spikes: WHS personnel prepared the Quality Assurance spikes for this study since the Center for Analytical Chemistry (CAC) Quality Assurance personnel (QA) were unavailable at the time. The resin beds of fourteen resin tubes (SKC Lot # 499) were spiked with 10 uL of a 5 ng/uL (each) Endosulfan I and II spike solution to yield 50 ng (each) Endosulfan I and Endosulfan II QA spikes. (The total was 100 ngs of Endosulfan I and II.) The tubes were allowed to stand for one hour and then the broken ends of the primary sections were capped.

Standards of Endosulfan I and II were secured from CAC Standards Repository and the Spike Solution Numbers were 215-3309a and 216-3311b respectively.

Two spikes were analyzed for spiking level verification. Four spikes were retained in the lab in Freezer # 27873 as Lab spikes. The remaining eight spikes were given to ARB staff members to use as Trip spikes and Field spikes. When they were returned to the lab, all 12 QA spikes were extracted and analyzed at the same time. The following table lists the % recovery.

TABLE 5. QA SPIKES--% Recovery at 50 ng each component

ARB ID	% Recovery Endosulfan I	% Recovery Endosulfan II
QA-LS-1	89.86	66.42
QA-LS-2	79.87	57.50
QA-LS-3	79.60	60.30
QA-LS-4	81.40	62.30
QA-FS-1	84.20	60.78
QA-FS-2	89.60	65.22
QA-FS-3	83.84	61.28
QA-FS-4	81.34	59.68
QA-TS-1	83.08	60.00
QA-TS-2	80.38	57.10
QA-TS-3	86.62	66.16
QA-TS-4	78.30	58.94

Please see Attachment G1➢ G3 for resin Lab, Trip and Field spike chromatograms.

5. QUALITY CONTROL:

A. Collection efficiencies and storage stability: For collection efficiencies and storage stability data, please refer to the method SOP as supplied by ARB (Attachment B).

B. Resin sample/extract integrity: Once received in the lab, all of the resin samples and spikes were stored in Freezer # 27873. The temperature of this freezer is recorded manually every work day. The average temperature of this freezer during the storage of samples and spikes was -16 ° C. At no time did the temperature vary more than +/- 3 ° C. In all cases, the resin samples and spikes were analyzed on the same day that they were extracted.

C. On-going Quality Control spikes: The following table lists the WHS Laboratory on-going QC spike recoveries The resin tubes were spiked with 150 ng each Endosulfan I, II and Sulfate. Please see Attachment H for a resin spike chromatogram.

TABLE 6. WHS LABORATORY ON-GOING QC Spikes--% Recovery at 150 ng each

Date Analyzed	Lab ID	Sample ID	% Recovery Endosulfan I	% Recovery Endosulfan II	% Recovery Endosulfan Sulfate
4-21-97	421-A	Resin spike	86.67	68.67	53.33
4-21-97	421-B	Resin spike	89.33	70.67	58.10
5-1-97	501-A	Resin spike	89.33	66.00	51.30
5-1-97	501-B	Resin spike	88.33	68.00	51.33

D. On-going Quality Control blanks: The following table lists the results of the resin blanks that were analyzed as part of the WHS Laboratory on-going QC for this Endosulfan study. Please see Attachment I for a chromatogram for a resin blank sample.

TABLE 7. WHS LABORATORY ON-GOING QC RESIN BLANK RESULTS

Date Analyzed	Lab ID	Sample ID	Endosulfan I	Endosulfan II	Endosulfan Sulfate
4-21-97	421-C	Blank	N. D.	N. D.	N. D.
5-1-97	501-C	Blank	N. D.	N. D.	N. D.

6. DISCUSSION:

Please see Attachment J for a chromatogram of an ARB Endosulfan resin sample.

ATTACHMENT A1

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

ENDOSULFAN APPLICATION
CHAIN OF CUSTODY

SAMPLE RECORD

Job #: C97-004

Date: 4/17/97
Sample/Run #:
Job name: Endo - Appl.
Log numbers: 1-8

ACTION			INITIALS		METHOD OF STORAGE
Sample Collected			KEM		freezer, ice or dry ice
	DATE	TIME	GIVEN BY	TAKEN BY	
Transfer	4/7/97		KEM	NTA	
Transfer	4/7/97	0900	NTA	SM	
Transfer					
Transfer					
Transfer					
Transfer					

	LOG #	ID #	DESCRIPTION
WHSC 83	1	ENDEB	
cac 17	2	ENDEFS1	
84	3	ENDNB	
cac 18	4	ENDNFS2	
85	5	ENDWB	Samples
cac 19	6	ENDNFS3	
86	7	ENDSB	
cac 20	8	ENDSFS4	
	QA-TRIP	QATS-1to4	1-4
	SPIKES	.	

RETURN THIS FORM TO: Kevin Mongar (916) 263-2063

Samples stored in freezer # 27873 4-7-97 SM

ATTACHMENT A2

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

ENDOSULFAN APPLICATION
CHAIN OF CUSTODY

SAMPLE RECORD

Job #: C97-004

Date: 4/11/97
Sample/Run #:
Job name: ENDO
Log numbers: 13-32

ACTION			INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
	DATE	TIME	GIVEN BY	TAKEN BY	
Transfer	4-11-97	0930	NJA	S Maggio	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

	LOG #	ID #	DESCRIPTION
WHSC			
87, 88	13 14	ENDB2 SB2	
89, 90	15 16	WB2 NB2	
91, 92	17 18	ENDW1 S1	
93, 94	19 20	S1D E1	
95, 96	21 22	N1 ENDW2	
97, 98	23 24	S2 S2D	
99, 100	25 26	E2 N2	
101, 102	27 28	ENDW3 S3	
103, 104	29 30	S3D E3	
105, 106	31 32	N3 ENDBlk	

RETURN THIS FORM TO: Kevin Mongar (916) 263-2063

Samples stored in freezer # 27873. Inv 4-11-97

ATTACHMENT A3

CALIFORNIA AIR RESOURCES BOARD
MONITORING & LABORATORY DIVISION
P.O. Box 2815, Sacramento CA 95812

ENDOSULFAN APPLICATION
CHAIN OF CUSTODY

SAMPLE RECORD

Job #: C97-004

Date: 4/11/97
Sample/Run #:
Job name: ENDO
Log numbers: 34-51

ACTION			INITIALS		METHOD OF STORAGE freezer, ice or dry ice
Sample Collected					
	DATE	TIME	GIVEN BY	TAKEN BY	
Transfer	4-11-97	0930	NMA	Sylvia Quick	
Transfer					
Transfer					
Transfer					
Transfer					
Transfer					

	LOG #	ID #	DESCRIPTION
WHSC	33	[illegible] S4	
107, 109	34	S4D	
109, 110	35	E4	
	36	N4	
111, 112	37	ENDWS	
	38	S5	
113, 114	39	S5D	
	40	E5	
115, 116	41	N5	
	42	ENDW6	
117, 118	43	S6	
	44	S6D	
119, 120	45	E6	
	46	N6	
121, 122	47	ENDW7	
	48	S7	
123, 124	49	S7D	
	50	E7	
125, [illegible]	51	N7	

RETURN THIS FORM TO: Kevin Mongar (916) 263-2063

Samples stored in freezer # 27873. SM 4-11-97

State of California
Air Resources Board
Monitoring and Laboratory Division/ELB

Standard Operating Procedure for the Analysis of Endosulfan in Ambient Air

1. SCOPE

This is a gas chromatography/electron capture method for the determination of endosulfan from ambient air samples. The method was adapted from J&W Scientific GC Chromatograms, Chlorinated pesticides, 1994-95 Catelogue, p120.

2. SUMMARY OF METHOD

The exposed XAD-2 resin tubes (SKC #226-30-06) are stored in an ice chest or refrigerator until desorbed with 3 ml of isooctane. The injection volume is 2 ul. A gas chromatograph with a DB-608 capillary column and an electron capture detector is used for analysis.

3. INTERFERENCES/LIMITATIONS

Method interferences may be caused by contaminants in solvents, reagents, glassware and other processing apparatus that can lead to discrete artifacts or elevated baselines. A method blank must be done with each batch of samples to detect any possible method interferences.

It has been noted that when high concentrations of endosulfan are injected, often a significant amount remains in the needle and results in carry over to the next injection. For this reason all injections should be done at least in duplicate. If significant carry over is observed, the run should be repeated.

4. EQUIPMENT AND CONDITIONS

A. INSTRUMENTATION:

Varian 3400 gas chromatograph
Varian 604 Data System
Varian 8200 Autosampler

Detector: 350°C
Injector: 250°C
Column: J&W Scientific DB-608, 30 meter, 0.32 mm i.d., 0.5 um film thickness.

Program: Initial 80°C, hold 1 min, to 265°C @ 50°C/min., hold 25 min. Retention times: Endosulfan I = 13.8 min., Endosulfan II = 17.8 min., Endosulfan sulfate = 20.8 min. End of run = 29.7 min.

Splitter open @ 0.8 min., flow 50 mL/min.

Flows:
column: He, 1.7 mL/min, 8 psi
Make up = 30 mL/min. N_2

B. AUXILIARY APPARATUS:

1. Glass amber vials, 8 mL capacity.
2. Vial Shaker, SKC, or equiv.
3. Autosampler vials with septum caps.

C. REAGENTS

1. Isooctane, Pesticide Grade, or better
2. Endosulfan I and II (alpha and beta isomers), Endosulfan sulfate 98% pure or better (Chem Service).

5. ANALYSIS OF SAMPLES

1. It is necessary to analyze a solvent blank with each batch of samples. The blank must be free of interferences. A solvent blank must be analyzed after any sample which results in possible carry-over contamination.

2. If a standard curve is not generated each day of analysis, at least one calibration sample must be analyzed for each batch of ten samples. The response of the standard must be within 10% of previous calibration analyses.

3. Carefully score the primary section end of the sampled XAD-2 tube above the retainer spring and break at the score. Remove the glass wool plug from the primary end of the XAD-2 tube with forceps and place it into an 8 mL amber colored sample vial. Pour the XAD-2 into the vial and add 3.0 mL isooctane. Retain the secondary section of the XAD-2 tube for later analysis to check the possibility of breakthrough.

4. Place the sample vial on a desorption shaker for 25 minutes. Remove the isooctane extract and store in a second vial at 4°C until analysis.

5. After calibration of the GC system, inject 2.0 ul of the extract. If the resultant peaks for endosulfan have a measured area greater than that of the highest standard injected, dilute the sample and re-inject.

6. Calculate the concentration in ng/mL based on the data system calibration response factors. If the sample has been diluted, multiply the calculated concentration by the dilution factor.

7. The atmospheric concentration is calculated according to:

Conc., ng/m^3 = (Extract Conc., ng/mL X 3 mL) / Air Volume Sampled, m^3

6. QUALITY ASSURANCE

A. INSTRUMENT REPRODUCIBILITY

Six replicate injections of 2 uL each were made of a standard containing all three of the endosulfans in order to establish the reproducibility of this instrument. This data is shown in TABLE 1.

TABLE 1. INSTRUMENT REPRODUCIBILITY

AMOUNT INJECTED (ng/mL)	Endosulfan I	Endosulfan II	Endosulfan sulfate
1.0	17,953 ± 450 (±3%)	11,662 ±1494 (±13%)	15,235± 1,288 (±8%)
5.0	50,537 ± 739 (+2%)	37,134 ±779 (±2%)	38,742 ±2,429 (±6%)
25.0	383,214 ± 14,464(±4%)	329,052 ±17,357 (±6%)	300,835 ±21,662 (± 7%)
50.0	714,243 ± 4,330 (±1%)	616,688 ±9,200 (± 2%)	614,554 ±14,658 (±2%)

B. LINEARITY

A four point calibration curve was made ranging from 1.0 ng/mL to 50.0 ng/mL (from TABLE 1). The coresponding equations and correlation coefficients are:

Endosulfan I $y = 6.8599 \times 10^{-5} X + 0.2543$ Corr. = .998

Endosulfan II $y = 7.9079 \times 10^{-5} X + 0.8138$ Corr. = .999

Endosulfan sulfate $y = 8.0121 \times 10^{-5} X + 0.8334$ Corr. = .999

C. MINIMUM DETECTION LIMIT

Using the equations above and the data below, the minimum detection limit for Endosulfan was calculated by:

$$MDL = |i| + 3(s.d._{low})$$

where: $|i|$ = the absolute value of the intercept of the standard curve (from above).

$s.d._{low}$ = the standard deviation of the lowest concentration used for the standard curve.

For Endosulfan I: lowest concentration used = 1.0 $\pm$ 0.29 ng/mL

MDL = |0.2543| + 3(0.29) = 1.12 ng/mL

For Endosulfan II: lowest concentration used = 1.0 $\pm$ 0.93 ng/mL

MDL = |0.8138| + 3(0.93) = 3.6 ng/mL

For Endosulfan sulfate: lowest concentration used = 1.0 $\pm$ 0.94 ng/mL

MDL = |0.8334| +3(0.94) = 3.7 ng/mL

Based on the 3 mL extraction volume and assuming a sample volume of 2.7 m^3 (1.9 lpm for 24 hours):

Endosulfan I: $\frac{1.12\ ng/mL\ (3\ mL)}{2.7\ m^3}$ = 1.2 ng/m^3 per 24-hour sample

Endosulfan II: $\frac{3.6\ ng/mL\ (3\ mL)}{2.7 m^3}$ = 4.0 ng/m^3 per 24-hour sample

Endosulfan sulfate: $\frac{3.7\ ng/mL\ (3\ mL)}{2.7\ m^3}$ = 4.1 ng/m^3 per 24-hour sample

D. COLLECTION AND EXTRACTION EFFICIENCY (RECOVERY)

Collection and extraction efficiency data for Endosulfan on XAD-2 is presented in TABLE 2.

TABLE 2. COLLECTION AND EXTRACTION EFFICIENCY FOR ENDOSULFAN ON XAD-2

ENDOSULFAN I			ENDOSULFAN II			ENDOSULFAN SULFATE		
Amount Spiked (ng)	Amount Recovered (ng)	(%)	Amount Spiked (ng)	Amount Recovered (ng)	(%)	Amount Spiked (ng)	Amount Recovered (ng)	(%)
50.0	50.4	101 ± 1	50.0	40.5	81 ± 3	50.0	34.4	69 ± 4
150	134.3	90 ± 1	150	106.4	71 ± 1	150	9105	61 ± 2

The standards were spiked on the primary section of an XAD-2 tube. The tube was then subjected to an air flow of approximately 2 lpm for 24 hours. The tubes were run at an ambient temperature of approximately 85°F. The primary sections were then desorbed with 3.0 mL of isooctane and analyzed by capillary column GC/ECD.

E. STORAGE STABILITY

Storage stability studies were done in triplicate for 1.0 ng endosulfan spikes on XAD-2 tube primary sections over a period of 20 days. The percent recovery data for storage stability is presented in TABLE 3.

TABLE 3. ENDOSULFAN STORAGE STABILITY AT 4°C

50 ng each spiked	PERCENT RECOVERY			
	0 DAY	2 DAYS	7 DAYS	20 DAYS
Endosulfan I	95±2	102±1	105±2	103±1
Endosulfan II	84±5	81±1	87±3	89±3%
Endosulfan Sulfate	79±6	72±1	80±4	86±7%

F. BREAKTHROUGH

Triplicate tubes were spiked at 50, 100 and 500 ng/tube (Endosulfan I, Endosulfan II and Endosulfan sulfate) then run for 24 hours at approximately 2 lpm, prior to analysis. No endosulfan was detected in the secondary of any of the tubes.

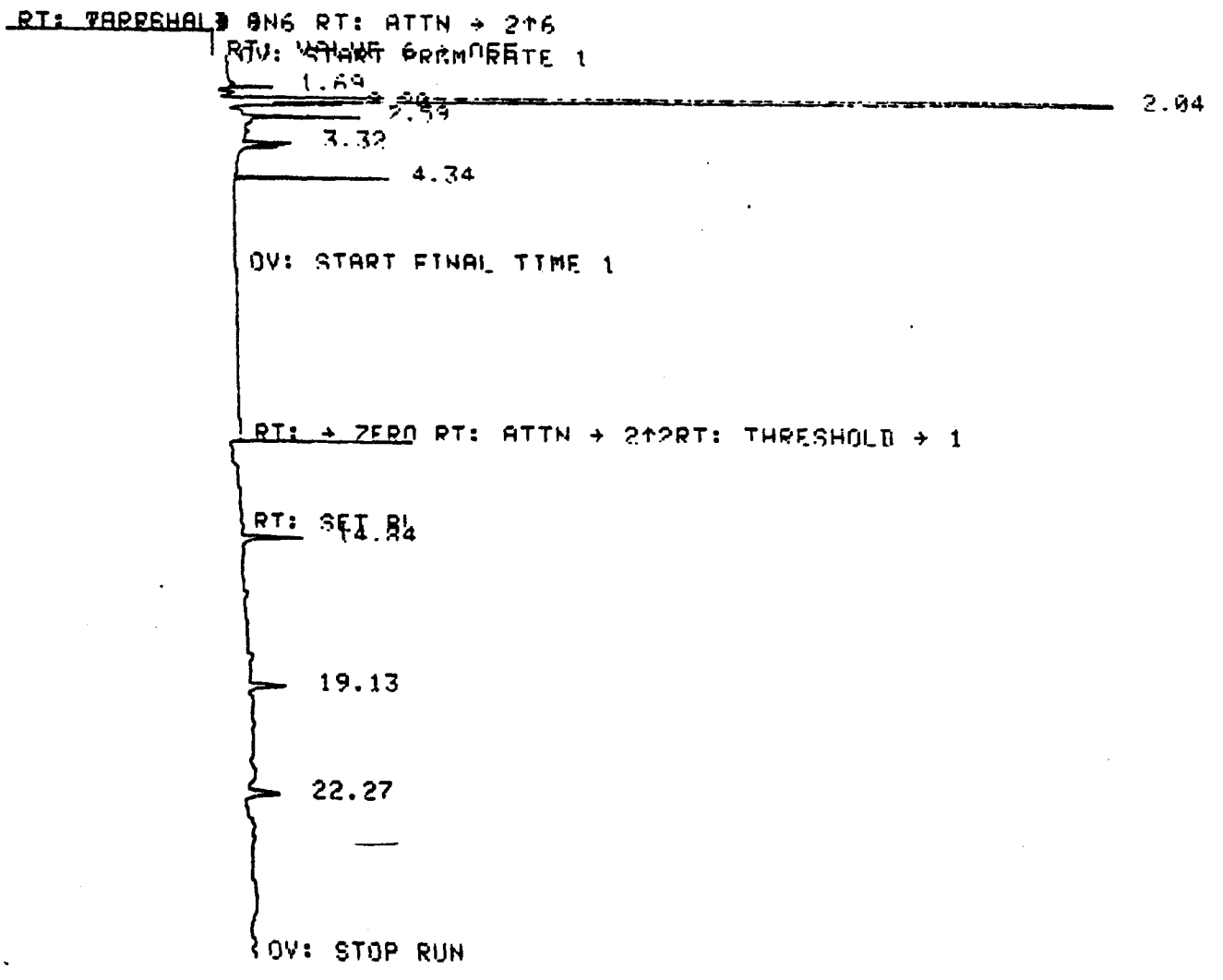
ESTD

ATTACHMENT C
MDL Verification Standard Chromatogram - 0.004 ug

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
20.47	37.60	BV		56.397	
21.33	0.11	BB		0.160	
21.49	0.26	BP		0.387	

MULTIPLIER = 1.5

OVEN TEMP NOT READY



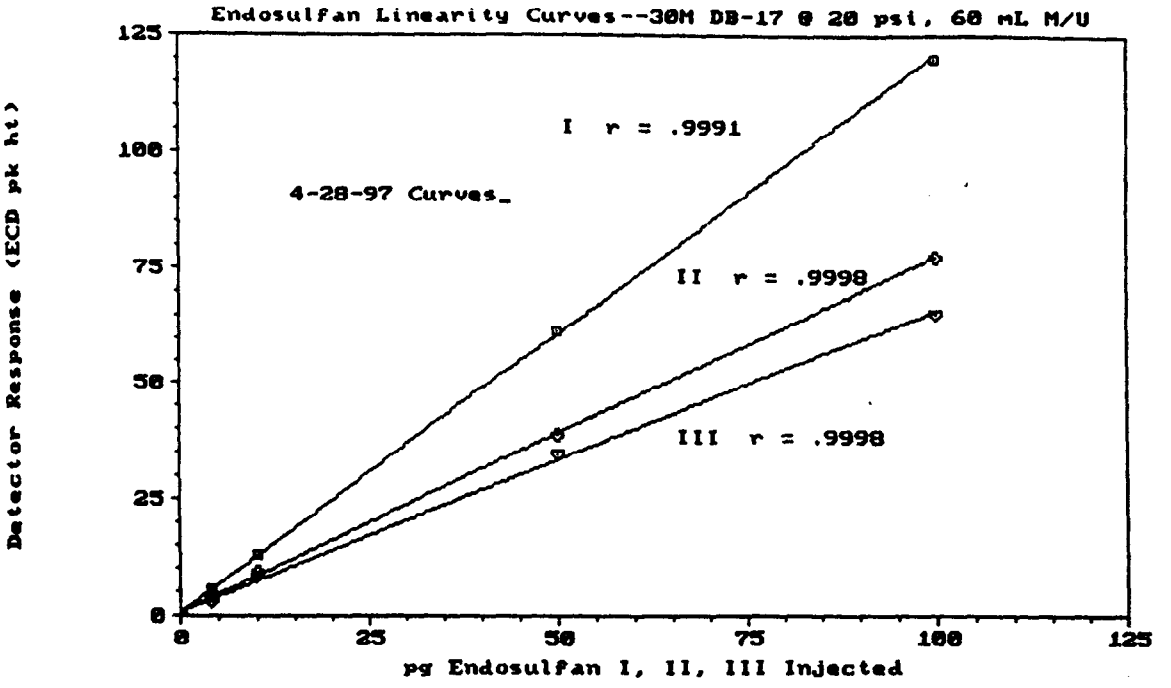
--RECALIB 1 --

--- AMOUNT UNITS ARE NG ANALYTE (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

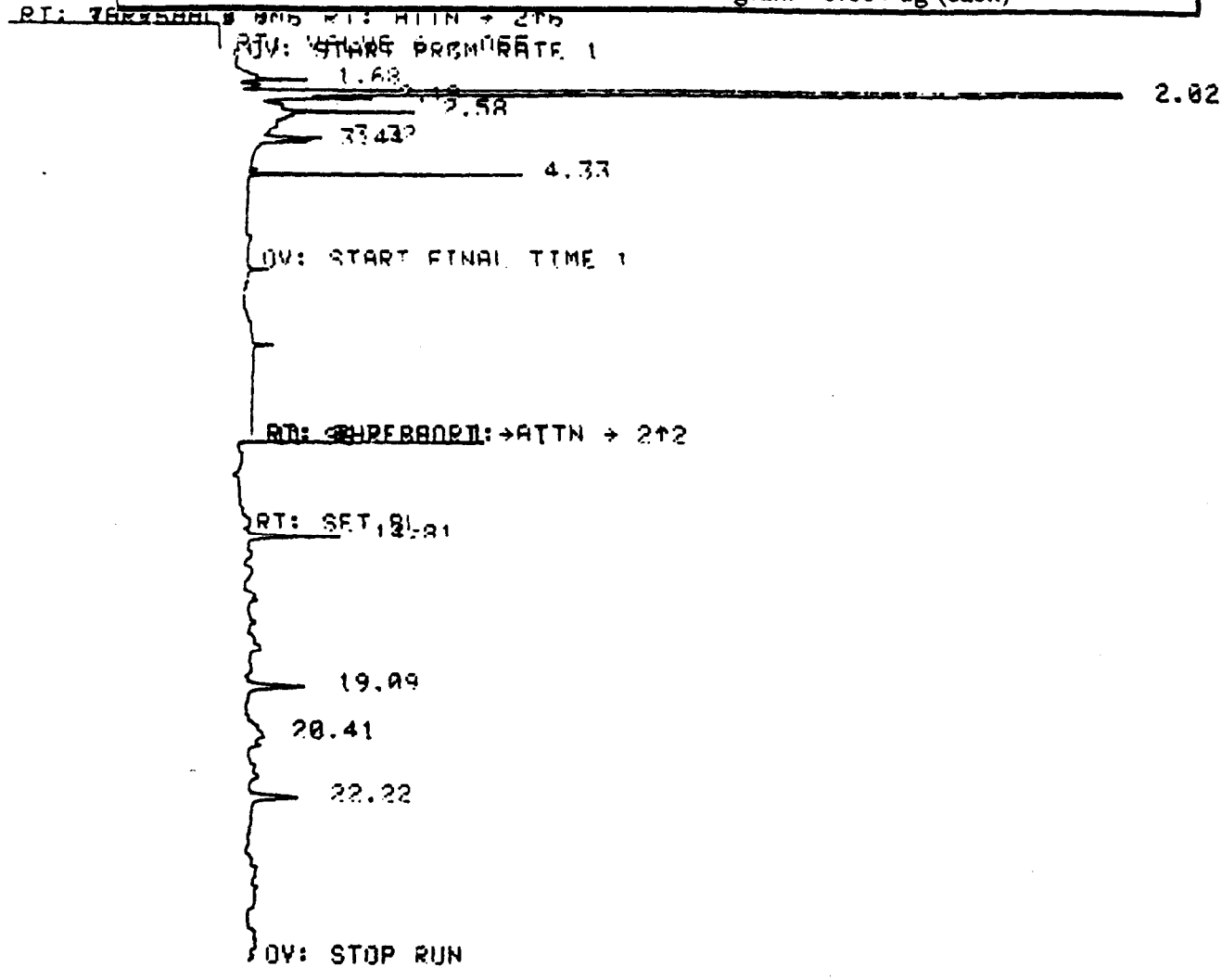
[hp] 5880A SAMPLER INJECTION @ 20:11 APR 22, 1997
SAMPLE # : ID CODE :
91 4 PG STD
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S@250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.84	3.98	PP	1	4.000E-03	ENDO I
19.13	2.42	BB	2	4.000E-03	ENDO II
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

ATTACHMENT D
Standard Curve Plotted r-Values



ATTACHMENT E-1
Standard Curve Chromatogram - 0.004 ug (each)



NO7

--RECALIB 1 --

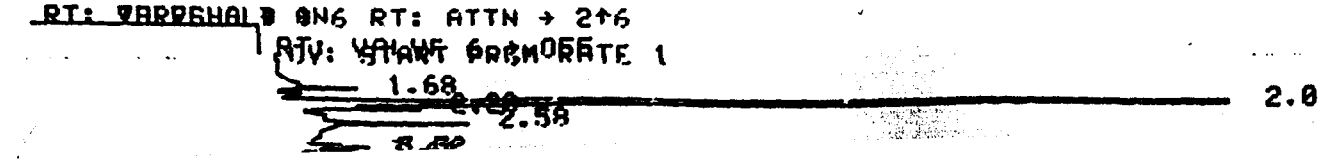
--- AMOUNT UNITS ARE NG ANALYTE (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

[hp] 5880A SAMPLER INJECTION @ 22:49 APR 24, 1997
SAMPLE # : ID CODE
91 4 PG STD
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S@250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.81	5.90	BV	1	4.000E-03	ENDO I
19.09	3.59	PR	2	4.000E-03	ENDO II
20.41	0.44	BP		0.436	
22.22	3.13	PB	3	4.000E-03	ENDO III

MULTIPLIER = 1

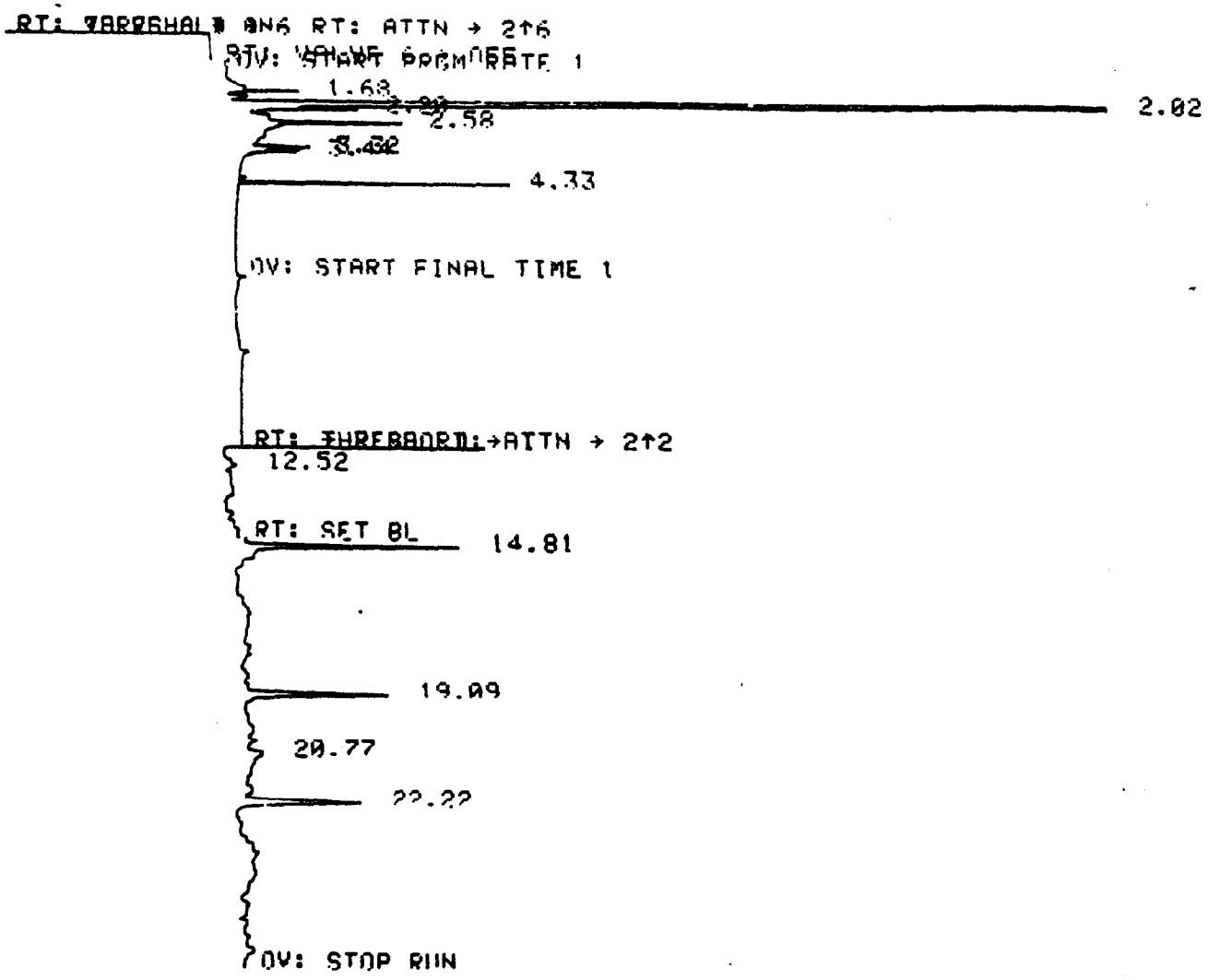
OVEN TEMP NOT READY



ATTACHMENT E-2
Standard Curve Chromatogram - 0.010 ug (each)

MULTIPLIER = 1

OVEN TEMP NOT READY



--RECALIB 2 --

--- AMOUNT UNITS ARE NG ANALYTE (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

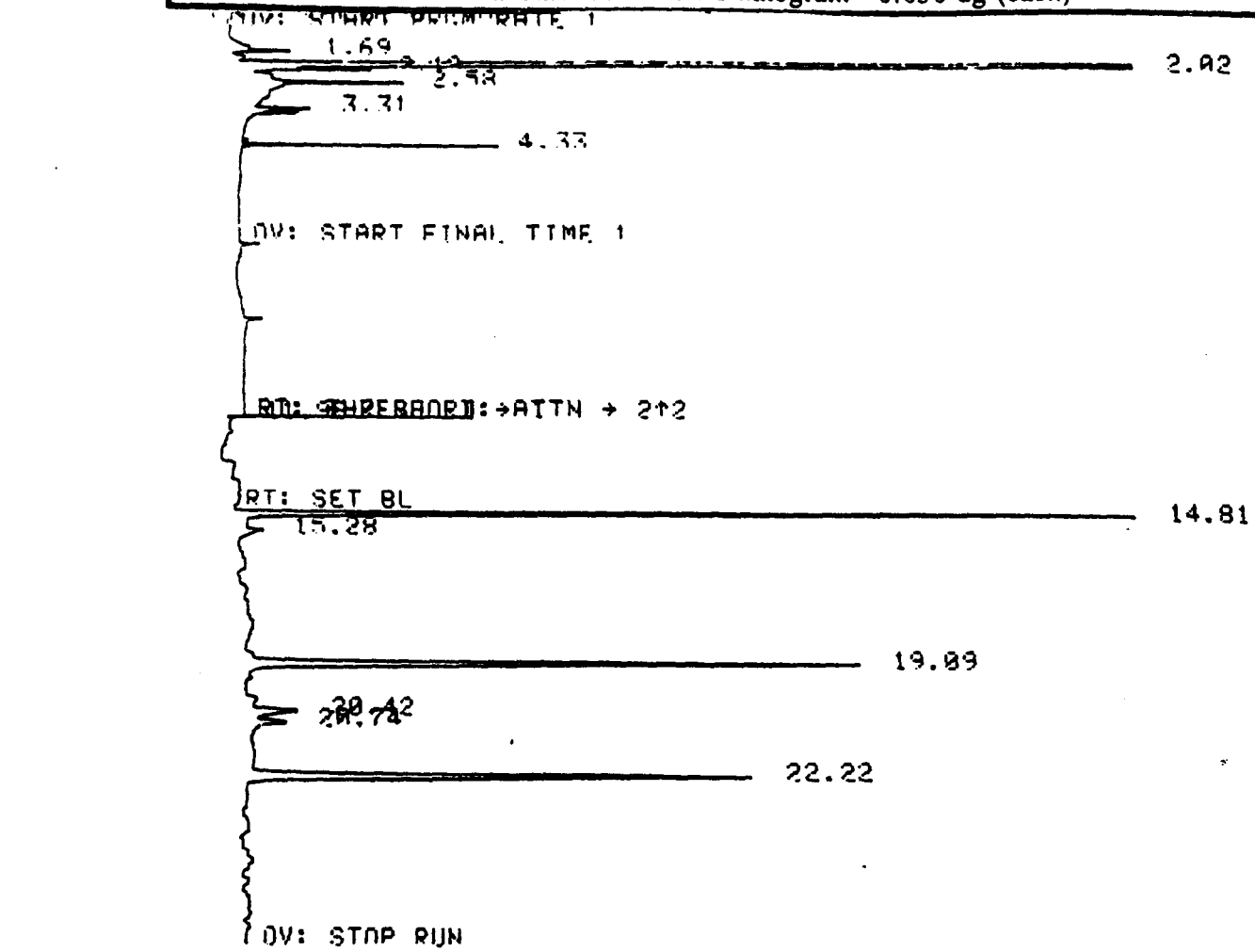
[hp] 5880A SAMPLER INJECTION @ 23:20 APR 24, 1997
SAMPLE # : ID CODE :
92 10 PG STD
ENDOSULFAN DB-17 30MX.25V 5 20PSI @0/1-260/30 M/U 60. S/S0250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.81	12.86	BB	1	1.000E-02	ENDO I
19.09	8.76	VB	2	1.000E-02	ENDO II
20.77	1.15	BV		1.147	.
22.22	7.59	VP	3	1.000E-02	ENDO III

MULTIPLIER = 1

OVEN TEMP NOT READY

ATTACHMENT E-3
Standard Curve Chromatogram - 0.050 ug (each)



--RECALIB 3 --

--- AMOUNT UNITS ARE NG ANALYTE (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

[hp] 5880A SAMPLER INJECTION @ 23:52 APR 24, 1997
SAMPLE # : ID CODE :
93 50 PG STD
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S0250
ESTD

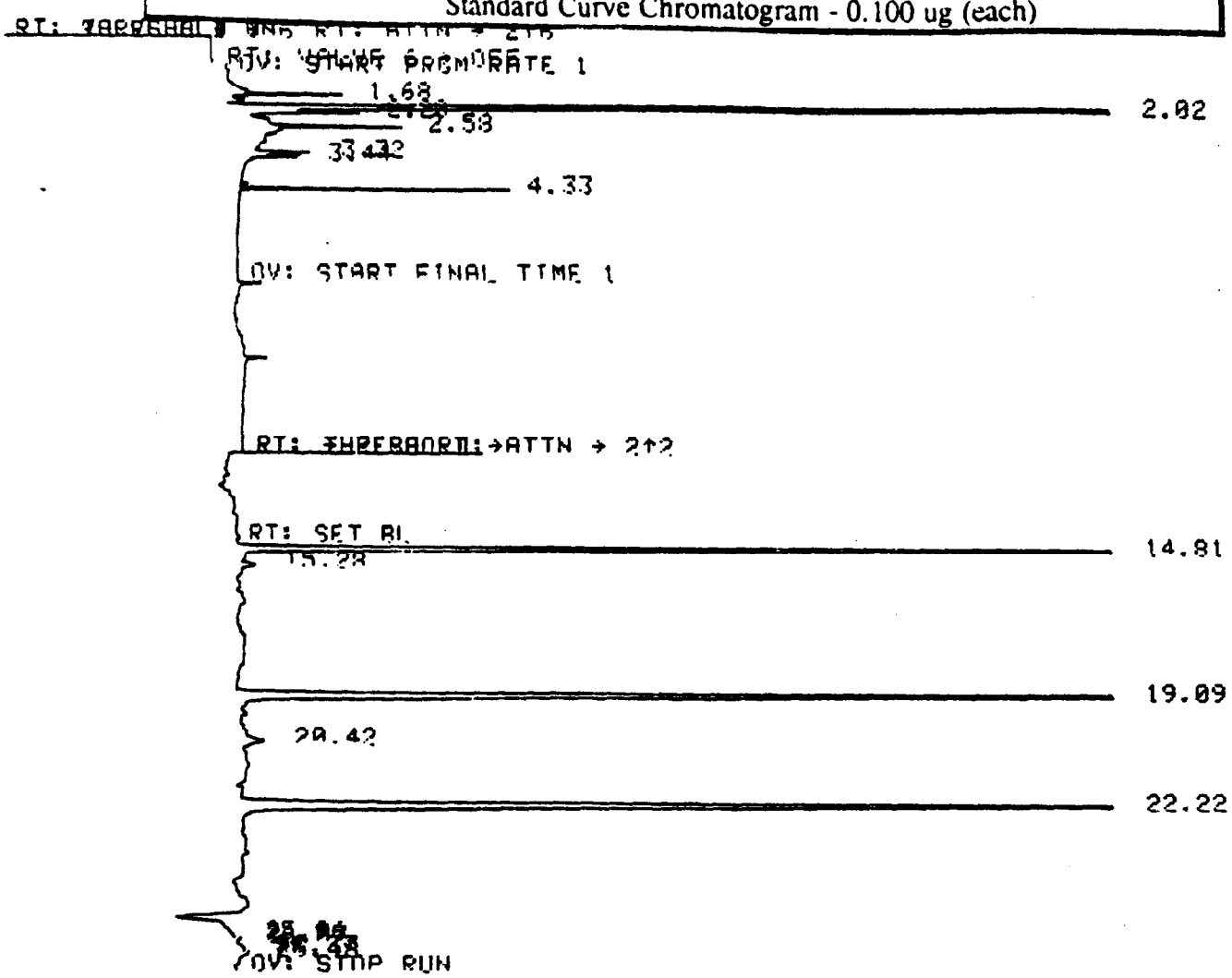
	RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
)	14.81	52.51	BV	1	5.000E-02	ENDO I
)	15.28	1.14	BB		1.138	
)	19.09	35.29	VP	2	5.000E-02	ENDO II
	20.42	2.78	BV		2.783	
	20.74	2.66	VB		2.663	
	22.22	29.18	BB	3	5.000E-02	ENDO III

MULTIPLIER = 1

OVEN TEMP NOT READY

RT: [illegible] ON6 RT: ATTN → 2↑6
OV: VALVE FROM OFF
OV: START PROM RATE 1
1.69

ATTACHMENT E-4
Standard Curve Chromatogram - 0.100 ug (each)



--RECALIB 4 --

--- AMOUNT UNITS ARE NG ANALYTE (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

[hp] 5880A SAMPLER INJECTION @ 00:24 APR 25, 1997
SAMPLE # : ID CODE :
94 100 PG STD
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/SR250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.81	114.94	BV	1	0.100	ENDO I
15.28	0.94	VB		0.942	
19.09	76.32	PB	2	0.100	ENDO II
20.42	1.29	BP		1.289	
22.22	64.53	BB	3	0.100	ENDO III
25.96	2.25	PV		2.249	
26.07	2.03	VV		2.027	
26.37	1.57	VV		1.574	
26.48	1.24	VB		1.245	

MULTIPLIER = 1

OVEN TEMP NOT READY

California Department of Food and Agriculture
Center for Analytical Chemistry
Worker Health and Safety Laboratory
3292 Meadowview Road
Sacramento, CA 95832

Number: WHS-AD-11
Date: 02/05/96
Revision:
Replaces:

STANDARD OPERATING PROCEDURE

Title: Data Generation and Reporting

Purpose: To Provide a Standardized Procedure for the Generation and Reporting of Chromatographic Data

Scope: All laboratory personnel.

Procedure:

Any conflict with instructions in the method or protocol must be resolved with senior staff, the study director, and documented before proceeding.

The number of standards used should adequately describe the standard curve shape. Typically this is 3-5 points spanning 1-2 orders of magnitude for linear systems. For non-linear systems, additional points or narrower concentration ranges may be needed. Calibration curves should include a data point near the instrument MDL of the compound(s), or a point that approximates the project LOD. All samples with responses higher than the upper limit of the standard curve must be diluted and reanalyzed.

The number and concentration of standards necessary to "'adequately describe" the curve shape depend on the type of curve fitting used for data analysis as well as the actual shape of the curve, which in turn depends on the detector used and the chemical being analyzed. In the case of point-to-point curve fitting (used by HP 5880 and 3396 integrators), the number of standards and their concentrations should be chosen so that the maximum quantitative error between a smooth curve and the point-to-point line, measured at the midpoint between consecutive standard levels, is 15% or less. Curve-fit errors in systems that can use quadratic functions (HP MSD, Varian Saturn) are much less, and consequently wider concentration ranges can be used.

In general, using peak heights for GC data will minimize errors because it reduces the effect of small leading or trailing peak interferences. For LC work, peak areas yield better data because of the tendency for LC peaks to widen and shorten during a run due to the effect of developing column voids.

Retention times should be reproducible to better than 1% in most cases for both LC and GC. Capillary GC and gradient LC times should be even better. Some systems will

slowly drift due to changing ambient conditions in the lab, but consecutive runs should show very small changes.

Samples must be run in groups small enough that the standard curves on either side of them will not vary by more than +/- 15%. Sufficient data should be generated during method development to provide guidance for the chemist on this number, and that information should be included in the method. Typically, no more than 10-20 samples should be analyzed between standard curves. 'Conditioning' samples and cooling GC analytical systems between batches may provide more consistent data.

Residues are generally reported in micrograms/sample. In the absence of complicating factors, levels should be reported as follows:

>= 1000 ugs	to nearest 10 ug
100 to 999 ugs	to nearest ug
10 to 99.9 ugs	to nearest 0.1 ug
1 to 9.99 ugs	to nearest 0.01 ug
0.010 to .999 ugs	to nearest 0.001 ug

To prevent confusion when reporting high levels of residue, do not mix reporting units. That is, do not report some values as ugs/sample, and some as mgs/sample within the same group of samples, unless the unit changes are ***clearly*** marked to draw the reader's attention.

Recovery data should be reported, but sample results NOT corrected for recovery. If corrected results are reported, a notation explicitly stating that fact should be included on the report sheet.

Reviewed By:

Terry Jackson, QA Officer
Center for Analytical Chemistry

Approved By:

7/12/96

Lilia Rivera, Program Supervisor
Center for Analytical Chemistry

Approved By:

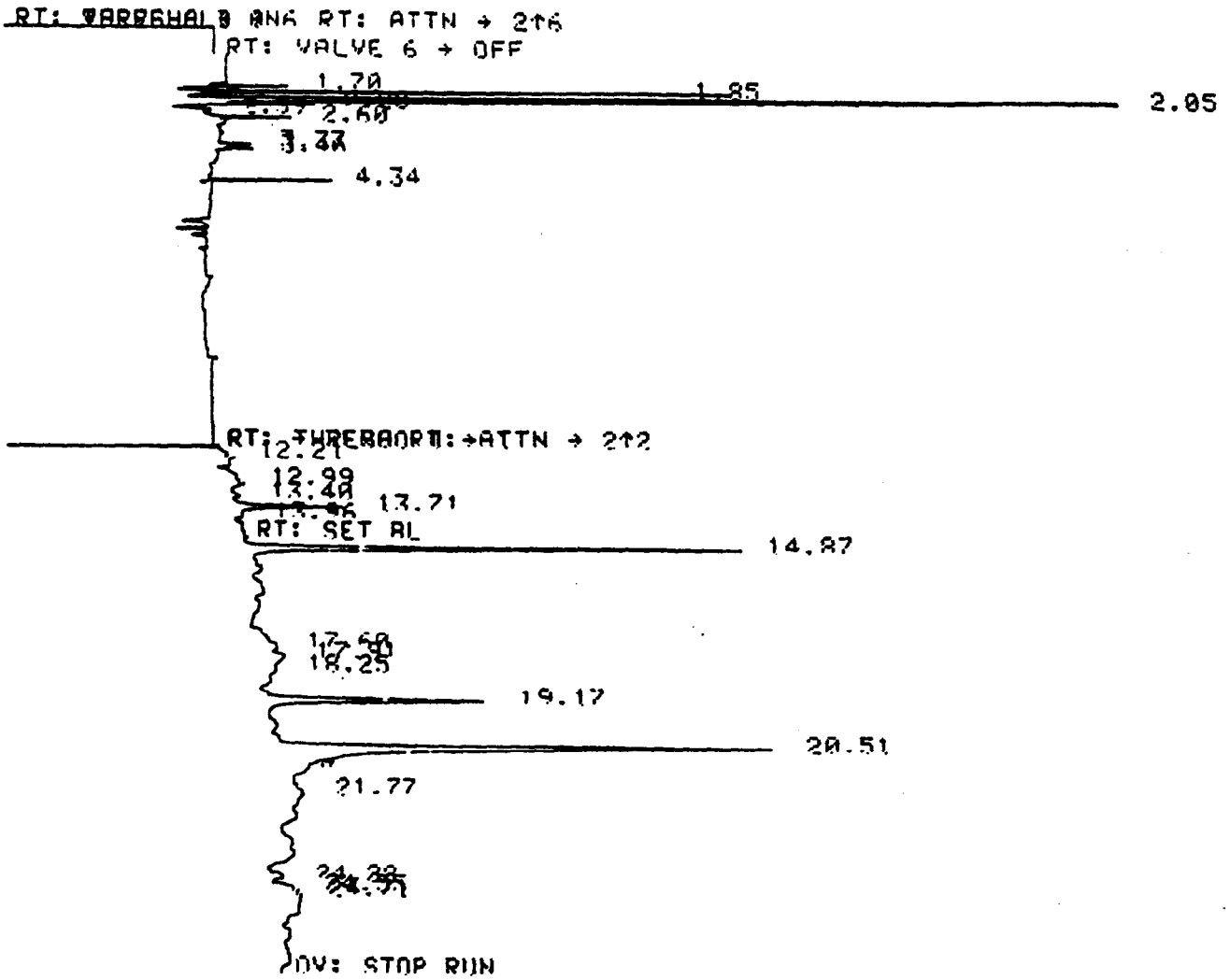
15 July 96

William Cusick, Chief
Center for Analytical Chemistry

ATTACHMENT G-1
Resin Lab Spike Chromatogram - 50 ng (each) Endosulfan I and II

MULTIPLIER = 1

OVEN TEMP NOT READY

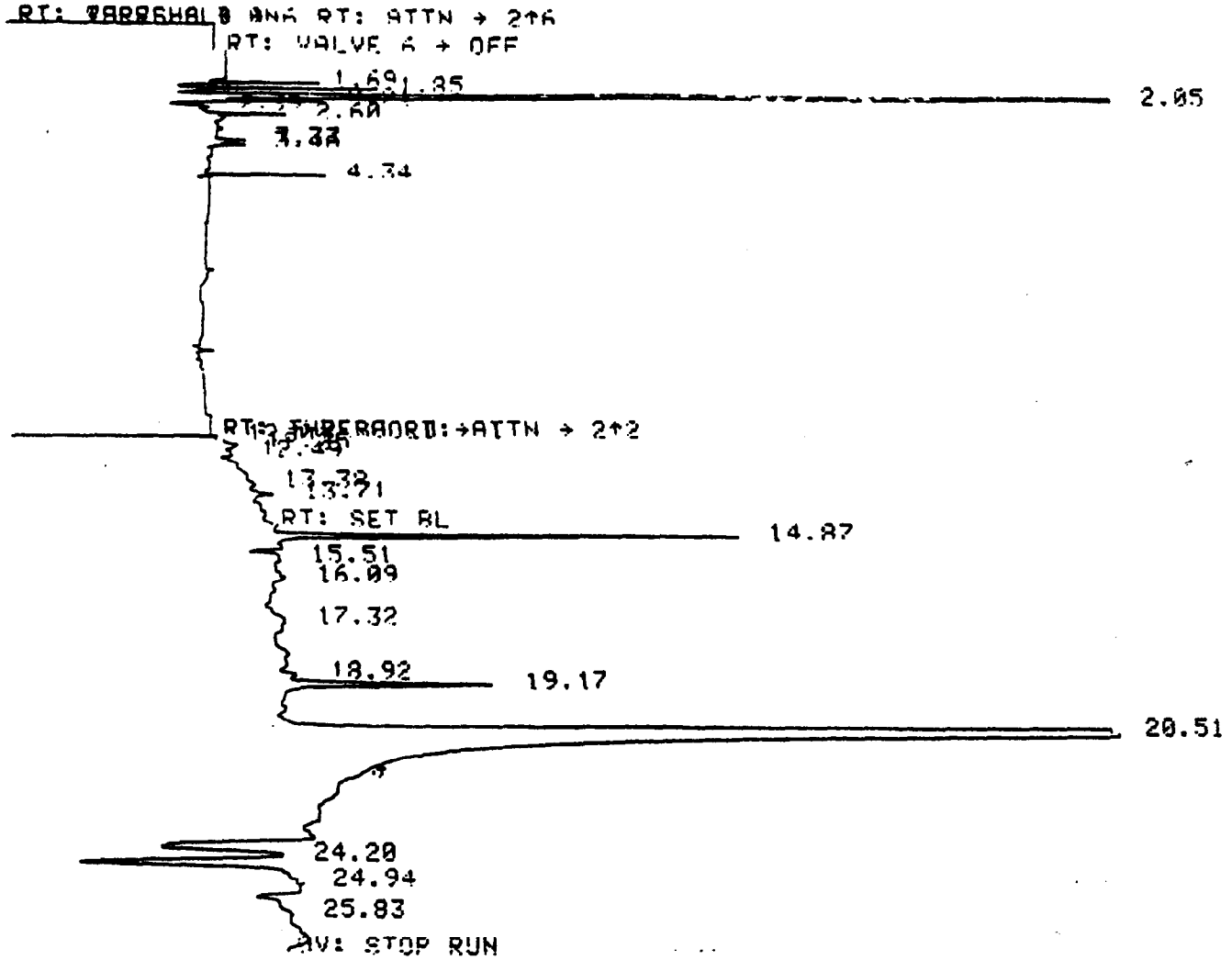


--- AMOUNT UNITS ARE ng/SPL (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2043A02086

[hR] 5880A SAMPLER INJECTION @ 18:28 APR 16, 1997
SAMPLE # : ID CODE :
21 QALS1.
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S@250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.87	28.57	BP	1	4.493E-02	ENDO I
17.60	0.34	BB		0.507	
17.91	0.59	BB		0.880	
18.25	0.24	BB		0.360	
19.17	13.06	PB	2	3.321E-02	ENDO II
20.51	28.91	PV		43.368	
21.77	0.20	BB		0.293	
24.28	1.12	BH		1.680	
24.55	1.80	HH		2.707	
24.71	2.00	HH		3.001	

ATTACHMENT G-2
Resin Trip Spike Chromatogram - 50 ng (each) Endosulfan I and II



--- AMOUNT UNITS ARE xG/SPL (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2043A02086

[hp] 5880A SAMPLER INJECTION @ 00:50 APR 17, 1997
SAMPLE # : ID CODE :
29 OATS-1
ENDOSULFAN 08-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S0250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.87	27.63	BV	1	4.154E-02	ENDO I
15.51	1.16	PB		1.747	
16.09	0.43	BB		0.640	
17.32	0.54	BB		0.813	
18.92	1.27	BV		1.907	
19.17	12.82	VB	2	3.001E-02	ENDO II
20.51	274.78	BV		412.167	
24.20	10.10	BP		15.149	
24.94	0.63	BV		0.947	
25.83	0.37	BB		0.560	

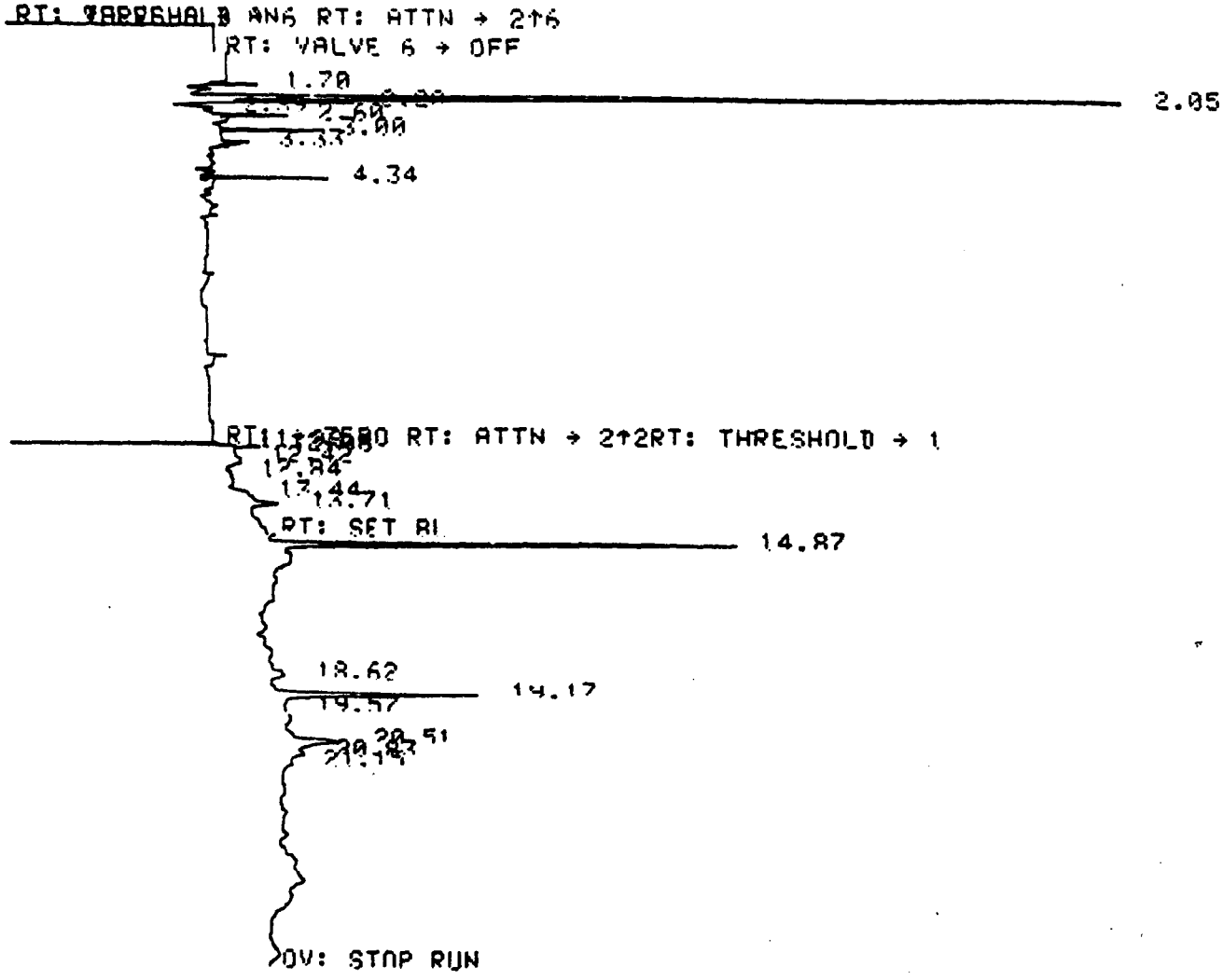
MULTIPLIER = 1.5

OVEN TEMP NOT READY

ATTACHMENT G-3
Resin Field Spike Chromatogram - 50 ng (each) Endosulfan I and II

MULTIPLIER = 1.5

OVEN TEMP NOT READY



--- AMOUNT UNITS ARE µG/SPL (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2043A02086

[hp] 5880A SAMPLER INJECTION @ 20:35 APR 16, 1997
SAMPLE # : ID CODE :
25 RAFS-1
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S@250
ESTD

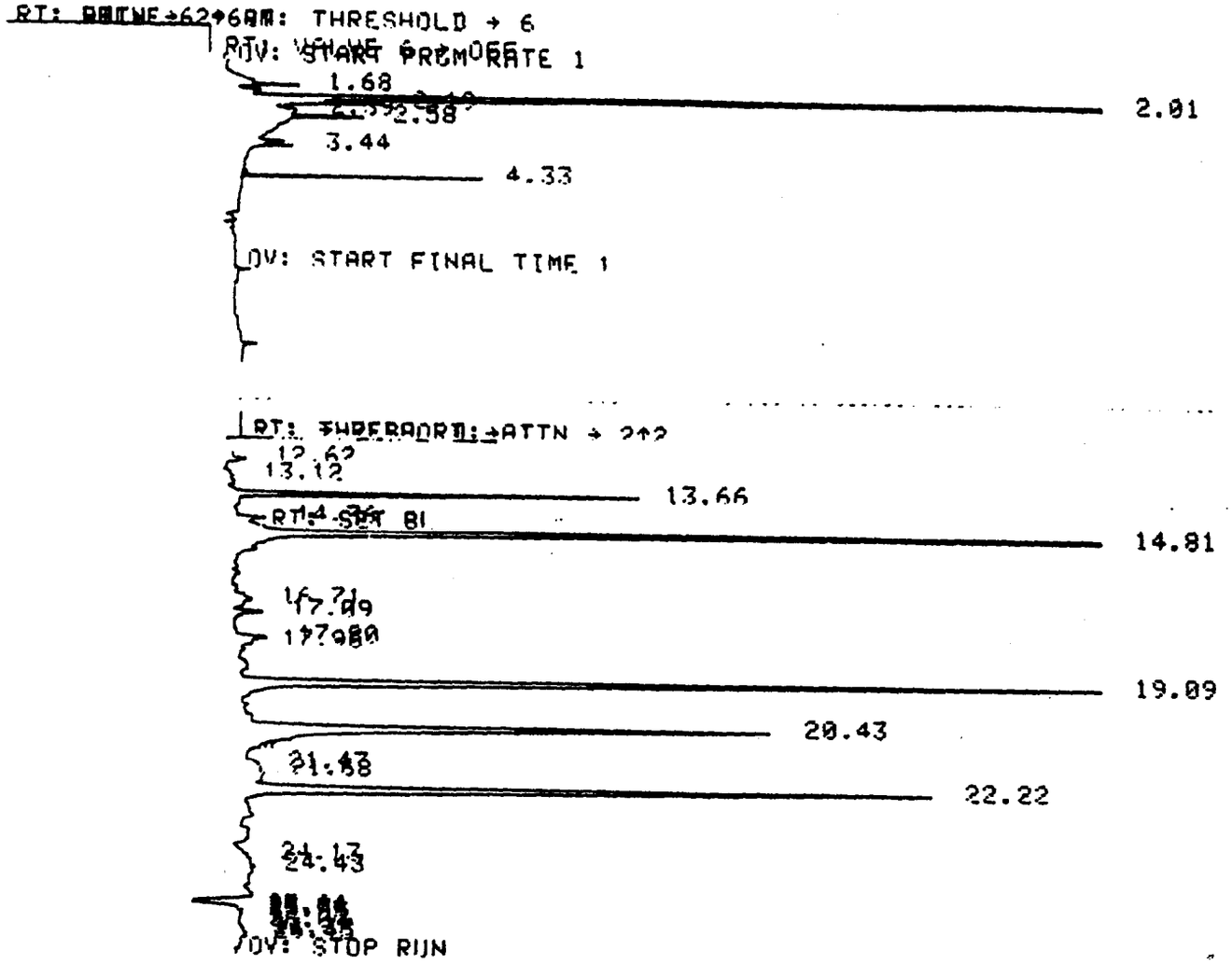
RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.87	26.88	BV	1	4.207E-02	ENDO I
18.62	0.95	BP		1.427	
19.17	12.06	BB	2	3.039E-02	ENDO II
19.57	0.25	BB		0.373	
20.51	3.05	BV		4.574	
20.83	1.03	VV		1.547	
21.15	0.48	VB		0.720	

MULTIPLIER = 1.5

OVEN TEMP NOT READY

ATTACHMENT H
Resin On-Going QC Spike Chromatogram

OVEN TEMP NOT READY

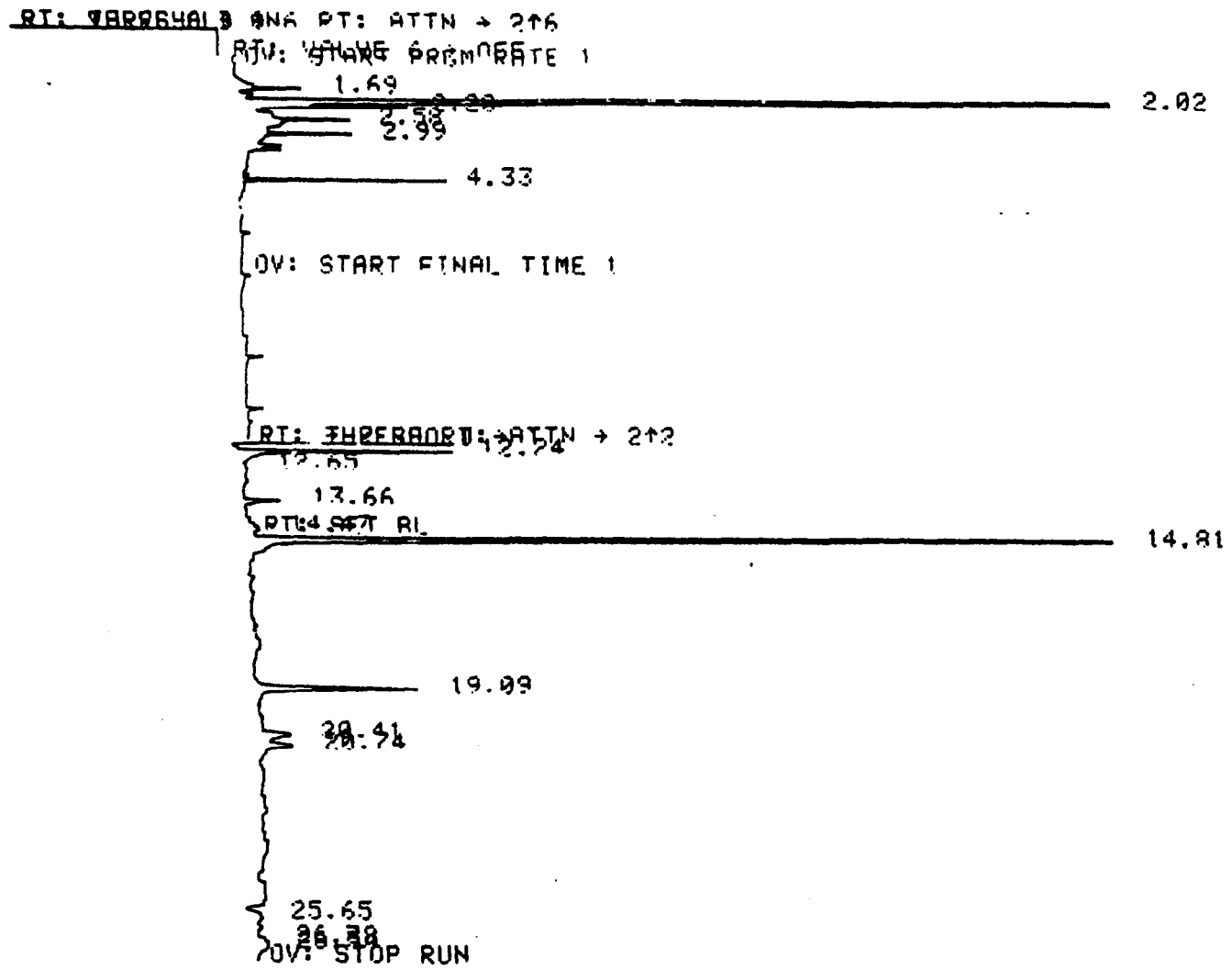


--- AMOUNT UNITS ARE NG/SPL (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

[hp] 5880A SAMPLER INJECTION @ 19:06 APR 24, 1997
SAMPLE # : ID CODE :
22 421 A SPK
ENDOSULFAN DB-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60. S/S@250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.36	1.67	PP		2.507	
14.81	114.14	BP	1	0.134	ENDO I
16.71	0.93	BB		1.400	
17.09	1.97	BB		2.961	
17.80	2.04	BV		3.054	
17.96	1.09	VV		1.640	
19.09	57.45	BV	2	0.101	ENDO II
20.43	30.93	BV		46.395	
21.47	0.72	BV		1.080	
21.68	0.75	VV		1.120	
22.22	40.42	BP	3	8.392E-02	ENDO III
24.13	0.41	BP		0.613	
24.43	0.58	BV		0.867	

OVEN TEMP NOT READY



--- AMOUNT UNITS ARE NG/SPL (CALIBRATED IN NG INJECTED) ---
HP 5880A S/N 2407A05786

[hp] 5880A SAMPLER INJECTION @ 01:28 APR 25, 1997
SAMPLE # : ID CODE :
32 C-91.
ENDOSULFAN D8-17 30MX.25X.5 20PSI 80/1-260/30 M/U 60, S/S@250
ESTD

RT	HEIGHT	TYPE	CAL	AMOUNT	NAME
14.47	0.67	A PV		1.000	
14.81	78.76	BB	1	0.107	ENDO I
19.09	0.93	BV	2	1.765E-02	ENDO II
20.41	1.78	PV		2.667	
20.74	1.93	VB		2.894	
25.65	0.44	BB		0.667	
26.38	0.59	BV		0.880	
26.54	0.55	VB		0.827	

MULTIPLIER = 1.5

OVEN TEMP NOT READY

APPENDIX III

QMOSB AUDIT REPORT

Cal/EPA

California
Environmental
Protection
Agency

Air Resources Board

P.O. Box 2815
2020 L Street
Sacramento, CA
95812-2815

Pete Wilson
Governor

Secretary for
Environmental
Protection

MEMORANDUM

TO: George Lew, Chief
Engineering and Laboratory Branch

THROUGH: Jeff Cook, Chief
Quality Management and Operations
Support Branch

FROM: Alice Westerinen, Manager
Quality Assurance Section

DATE: October 17, 1997

SUBJECT: FINAL ENDOSULFAN 1996 QA SYSTEM AUDIT REPORT

Attached is the final quality assurance system audit report on the endosulfan monitoring project conducted during September 1996, by the Engineering and Laboratory Branch of the Air Resources Board.

Thank you for participating in this audit. If you have any questions, please contact Mr. Trevor M. Anderson at (916) 323-0346.

Attachment

cc: Trevor M. Anderson
Kevin Mongar

STATE OF CALIFORNIA AIR RESOURCES BOARD

MONITORING AND LABORATORY DIVISION

QUALITY ASSURANCE SECTION

SYSTEM AUDIT REPORT

AMBIENT MONITORING OF ENDOSULFAN

IN

FRESNO COUNTY

FINAL

OCTOBER 1997

TABLE OF CONTENTS

ENDOSULFAN MONITORING
IN
FRESNO COUNTY

TABLES

ATTACHMENTS

I. EXECUTIVE SUMMARY

In September 1996, the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) conducted a six-week. source-impacted ambient air monitoring program for an application of endosulfan to a field in Fresno County. This monitoring was conducted to determine if endosulfan I (EDI), endosulfan II (EDII), and the breakdown product, endosulfan sulfate (EDS), could be detected and measured in ambient air. The samples were collected and analyzed by ELB.

The Quality Assurance Section (QAS) of ARB's Monitoring and Laboratory Division (MLD) conducted a system audit of the field and laboratory operations to review the sample handling and storage procedures, analytical methodology, and method validation. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

Additionally, QAS staff conducted performance audits of the air monitoring samplers. The performance audits of the air monitoring samplers were conducted to evaluate the flow rate accuracy. The flow rate audit was administered on July 17, 1996. The difference between the reported and assigned flow rates averaged 0.8% with a range of -8.0% to 7.1%.

To determine the effectiveness of the analytical procedure, laboratory performance audits were also performed. In August 1996, a total of 22 QA audit samples were spiked with known amounts of EDI, EDII, and EDS. These samples were submitted to ELB for analysis. The samples were prepared from EDI, EDII, and EDS standard solutions obtained from AccuStandard Inc. and Axact Standards Inc.

The 22 audit samples were designated as QA field spikes, QA trip spikes, and QA laboratory spikes. The QA field spikes were exposed to the same handling and storage conditions and also exposed to the same environmental and monitoring conditions as those occurring at the time of ambient sampling. The QA trip spikes followed the same handling and storage conditions of the ambient samples. Finally, QA laboratory spikes were stored at ELB's storage freezer and then analyzed at ELB laboratory.

The first set of seven QA spiked audit samples analyzed were QA laboratory spikes for EDI, EDII, and EDS. These samples were analyzed between August 30, 1996, and September 1, 1996. The audit results for EDI indicated a low recovery rate. The difference between the assigned and the reported total mass for EDI laboratory spikes averaged -74.1% with a range of -100% to -59.2%.

QAS staff reviewed the sample storage stability study, conducted by ELB, to determine the percent recovery of EDI, EDII, and EDS over time. The stability study used 50 nanograms (ng) of EDI, EDII, and EDS stored at 4° Celsius over a period of 20 days. The results of the stability study show EDI samples had a 103±1% recovery, EDII samples had a 89±3% recovery, and EDS samples had a 86±7% recovery over a period of 20 days. No breakthrough occurred during the 24 hours of dynamic sampling at 2 liters per minute (LPM) air flow.

The QAS staff, in conjunction with ELB, conducted an investigation to determine the cause of the low recovery results for EDI QA laboratory spikes. Staff was unable to find any inconsistencies with the sample solution, laboratory procedures, or spiking procedures. However, as part of the investigation, it was noticed that the storage of the spiked standard solutions procured by AccuStandard and Axact is handled differently between the manufacturers recommended storing condition and the approved ELB Standard Operating Procedures (SOP). The manufacturer recommends the AccuStandard and Axact standard solutions to be stored at room temperature, whereas ELB's SOP recommends the solution to be stored at 4° Celsius. However, if the standard solution is stored at the lower temperature, then appropriate equilibration is needed to bring the standard solution to room temperature before use.

QAS staff contacted representatives from both the Axact and AccuStandards laboratories to determine what, if any, this change of temperature could have on the spiked samples. The representatives stated, at the initial concentrations given, a failure to allow the solutions to equilibrate to 20° Celsius before spiking could allow absorption of the EDI, EDII, or EDS concentration to the glass container. If the spiked solution did adhere to the container poor results of the spiked samples would occur.

A second standard solution was prepared by ELB staff and compared to their working standard. This was prepared by ELB staff to determine the accuracy of their laboratory standard solution. In this comparison, ELB staff found no difference in standard solutions. It should be noted that in addition to this information, the laboratory standard concentration was created by using a pure or neat solution. This pure material is not dependant on temperature variations as is a diluted sample like the sample spiking solutions procured by AccuStandard and Axact. QA staff found no evidence to indicate the ambient results were affected by the temperature variations. Equilibration of the laboratory standards to room temperature was a standard operating practice in the analysis of all samples.

The QA laboratory audit results for EDII indicates a difference between the assigned and the reported total mass average of 4.6% with a range of -3.7% to 11.1%. For EDS, the audit results indicate a difference between the assigned and the reported total mass average of -28.7% with a range of -31.7 to -24.5%. After review and discussion with ELB staff, it was determined that QA laboratory spike data for both EDII and EDS were reasonable.

The next QA audit samples analyzed were ten QA trip spikes for EDI, EDII, and EDS. These samples were spiked using two different sets of standard solution. Of these sets, the first five samples were analyzed between October 3-4, 1996, using the standard solution from AccuStandard; the second five samples were analyzed between October 8-9, 1996, using the standard solution from Axact. The audit results for EDI indicated a low recovery rate using both the AccuStandard and Axact spikes. The difference for EDI between the assigned and the reported total mass for the five AccuStandard QA trip spikes averaged -94.9% with a range of -100% to -89.8%. The difference between the assigned and the reported total mass for the five Axact QA trip spikes averaged -82.6% with a range of -100% to -64.3%.

QAS staff, in conjunction with ELB, conducted an investigation to determine the cause of the low recovery results for EDI QA trip spikes. In December 1996, approximately three months after initial spiking, ELB staff conducted a "head-to-head" comparison for EDI, EDII, and EDS, and analyzed the lab standard solution against the standard solutions used by QA staff provided by AccuStandard and Axact. This comparison found that the AccuStandard was comparable with the lab standard while the Axact standard recovery rate was low by a factor of 10. However, the solutions used for spiking were stored differently from the manufacture's recommended storing conditions for three months before the head-to-head comparison was conducted. Axact Standards Inc. only guarantees their product if the temperature remains between 18 and 28° Celsius. Therefore, the head-to-head comparison does not provide a solution to the inconsistencies with the AccuStandard spikes. Based on the storage temperature issue noted above, it is a possibility that the Axact standard solution could have been compromised if the solution was not fully allowed to equilibrate to 20° Celsius before sampling.

Staff found no other inconsistencies with the sample solution, handling procedures, spiking procedures, and laboratory procedures, other than the storage issue noted above. Based on the low recovery results for EDI QA trip spikes and inconsistent sample storage procedures noted above, the impact on the ambient data cannot be determined at this time.

The QA trip spike audit results for EDII were also complicated. The AccuStandard values reported non-detect for the samples spiked, therefore, these samples were not reasonable. The Axact values indicate the difference between the assigned and the reported total mass of EDII averaged -27.8% with a range of -29.6% to -25.9%. For EDS, all spikes were assigned blanks and no contamination of the blanks were detected. After review and discussion with ELB staff, it was determined that QA trip data for EDII Axact spikes and EDS trip blanks were reasonable.

The five QA field spiked audit samples were analyzed for EDI, EDII, and EDS. These samples were analyzed between October 8-9, 1996. Again, the audit results for EDI indicated a low recovery rate. The difference between the assigned and the reported total mass for EDI field spikes averaged -55.9% with a range of -61.7% to -46.4%. Based on the low recovery results for EDI QA field spikes and the inconsistent sample storage procedures noted above, the impact on the ambient data cannot be determined at this time.

The QA field spike audit results for EDII indicates a difference between the assigned and the reported total mass average of -16.7% with a range of -18.5% to -14.8%. For EDS, all spikes were assigned blanks and no contamination was detected. After review and discussion with ELB staff, it was determined that QA field spike data for both EDII and EDS were reasonable.

II. CONCLUSION

Operations

The records for field operations, sample handling procedures, analytical methodology, and method validation were in agreement with the Quality Assurance Plan for Pesticide Monitoring.

Field Flow Rates

The results of the reported flow rates were in agreement with the actual flow rates measured by QAS staff.

Laboratory Accuracy

The QAS review of EDS laboratory spikes and blanks, trip blanks, and field blanks resulted in good recovery levels. The EDII laboratory spikes, field spikes, and all blanks resulted in good recovery levels. The results from the EDII trip spikes for QA-ET1 and QA-ET2 were not detected, so no

results were determined. Finally, the results of EDI spikes showed consistent recovery rates of -65%.

QAS staff, in conjunction with ELB, conducted an investigation to determine the cause of the low recovery results during the QAS analytical performance audit for laboratory, trip, and field spikes of EDI. Staff was unable to find any inconsistencies with the sample solution, laboratory procedures, or spiking procedures. However, as part of the investigation, it was noticed that the storage of the spiked standard solutions provided by AccuStandard and Axact is handled differently between the manufacturer's recommended storing condition and the approved ELB Standard Operating Procedures (SOP). The manufacturer recommends the AccuStandard and Axact standard solutions to be stored at room temperature, whereas ELB's SOP recommends the solution to be stored at 4° Celsius. However, if the standard solution is stored at the lower temperature, appropriate equilibration is needed to bring the standard solution to room temperature before use.

QAS staff contacted representatives from both the Axact and AccuStandards laboratories to determine what, if any, this change of temperature could have on the spiked samples. The representatives stated, at the initial concentrations given, a failure to allow the solutions to equilibrate to 20° Celsius before spiking could allow absorption of the EDI, EDII, or EDS concentration to the glass container. If the spiked solution did adhere to the container, poor results of the spiked samples would occur.

A second standard solution was prepared by ELB staff and compared to their working standard. This was prepared by ELB staff to determine the accuracy of their laboratory standard solution. In this comparison ELB staff found no difference in standard solutions. It should be noted that in addition to this information, the laboratory standard concentration was created by using a pure or neat solution. This pure material is not dependant on temperature variations as is a diluted sample like the sample spiking solutions procured by AccuStandard and Axact. QA staff found no evidence to indicate the ambient results were affected by the temperature variations. Equilibration of the laboratory standards to room temperature was a standard operating practice in the analysis of all samples.

In December 1996, approximately three months after initial spiking, ELB staff conducted a "head-to-head" comparison for EDI, EDII, and EDS, and analyzed the lab standard solution against the standard solutions used by QA staff provided by AccuStandard and Axact. This comparison found that the AccuStandard was comparable with the lab standard, while the

Axact standard recovery rate was low by a factor of 10. However, the solutions used for spiking were stored differently for three months from the manufacture's recommended storing conditions before the head-to-head comparison was conducted. Axact Standards Inc. only guarantees their product if the temperature remains between 18 and 28° Celsius. Therefore, the head-to-head comparison does not provide a solution to the inconsistencies with the AccuStandard spikes. Based on the storage temperature issue noted above, it is a possibility that the Axact standard solution could have been compromised if the solution was not fully allowed to equilibrate to 20° Celsius before sampling.

After reviewing QAS spiking standard solution handling, storage, and shipping records, along with records for analyses of QA spikes at ELB's laboratory, concentration for the standard solutions, stability studies, and all other laboratory and field procedures, and taking into account the temperature issue noted above, it has been determined that QAS analytical performance audit data for EDI produced consistent recovery rates of -65% for QAS spiking solution. This low recovery of the EDI spiked samples could be caused by the inconsistent sample storage procedures noted above. Based on the information provided, the impact on the ambient data compared with QAS spiking solution for EDI cannot be determined at this time.

III. RECOMMENDATIONS

1. Before handling and storing the standard solution, standard operating procedures should be checked against the recommended storing conditions by the manufacturer for any discrepancies.

2. Before handling and assembling the spiking solution and samples, laboratory procedures and practices should be thoroughly reviewed and followed by all parties involved.

3. Verify temperature requirements as well as concentrations of standard solutions before samples are spiked.

4. Additional precautions should be established to preclude the possibility of poor sample spiking.

IV. INTRODUCTION

In September 1996, the Engineering and Laboratory Branch (ELB) of the Air Resources Board (ARB) conducted a six-week source-impacted ambient air monitoring program for an application of endosulfan to a field in Fresno County. This

monitoring was conducted to determine if endosulfan I (EDI), endosulfan II (EDII), and the breakdown product, endosulfan sulfate (EDS), could be detected and measured in ambient air. The samples were collected and analyzed by ELB. The ARB's Monitoring and Laboratory Division's (MLD) Quality Assurance Section (QAS) staff conducted a system audit of the field and laboratory operations, and performance audits of the air samplers' flow rates and the analytical method.

V. AUDIT OBJECTIVE

The system audit was conducted to determine whether the quality control practices for the handling and storage of samples, analytical methodology, and method validation were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994). Performance audits were conducted to evaluate the accuracy of the air samplers' flow rates and the analytical method.

VI. FIELD AND LABORATORY OPERATIONS

A system audit of the field and laboratory operations was initiated in August 1996, through a questionnaire submitted to ELB staff. Additionally, the "Protocol for the Application Air Monitoring of Endosulfan in Fresno County During Fall, 1996" and ELB's "Standard Operating Procedure for the Analysis of Endosulfan in Ambient Air" were reviewed by QAS staff. In general, the laboratory practices were consistent with the Quality Assurance Plan for Pesticide Monitoring (ARB, February 4, 1994).

Ambient Air Sampling, Sample Handling and Storage

Samples were collected by drawing ambient air at measured rates through sample tubes containing XAD-2 resin. Once sampled, the exposed XAD-2 resin tubes were stored either on dry-ice or in a freezer until desorbed with 3 milliliters (mL) of isooctane in the laboratory. The flow rate was accurately measured and the sampling system operated continuously at the exact operating interval. The resin tube was protected from direct sunlight using a rain shield and was supported 1.5 meters above ground during the sampling period. An air sampler consisted of the Teflon cartridge connected with Teflon tubing to an in-line rotameter, which in turn was connected to an air pump. A sketch of the sampling apparatus is shown in Attachment 1.

The samplers' rotameters were set to an indicated flow rate of 2.0 LPM. The sampling was conducted following the schedule specified in the sampling protocol. The samples

were removed from the sample train, capped, and identification labels were affixed to each tube. Each tube was placed in a zip-lock plastic bag with up to five other samples. An identification label was then affixed to the zip-lock plastic bag. The samples were stored in culture tubes on dry ice and held in the field for up to one week prior to shipment to the laboratory. Upon receipt at ELB laboratory in Sacramento, the samples were either analyzed immediately or stored in a freezer until extraction and analyses were conducted. All samples were analyzed within the required two weeks of receipt by ELB.

Sample Analysis

The analytical method used was developed by ELB and described in the "Standard Operating Procedure for the Analysis of Endosulfan in Ambient Air." The method calls for the XAD-2 resin to be stored in a refrigerator or ice chest until desorbed with 3 mL of isooctane. The sample is desorbed by pouring the XAD-2 resin into a vial and adding 3 mL of isooctane. The sample is then placed on a shaker for 25 minutes. After being removed from the shaker, the sample is stored at 4° Celsius until analysis. A 2.0 microliter (μL) sample is then injected into the gas chromatograph (GC) and analyzed. The injected samples were analyzed on a Varian model 3400 gas chromatograph with a DB-608 capillary column and an electron capture detector. Four levels of EDI, EDII, and EDS standard concentrations (using a single injection per level) were used to establish the instrument standard calibration curve at 1 ng, 5 ng, 25 ng, and 50 ng.

The following quality control activities were performed to monitor and document the quality of the data: field control blanks were analyzed with every analytical run; laboratory spikes were analyzed in replicate with every analytical run; and about 10% of the samples were analyzed in replicate to document analytical precision. Precision checks of the data showed less than $\pm$10% difference. Field duplicates from collocated sites were collected once per week at each site. A portion of the samples were analyzed by Gas Chromatograph Mass Spectroscopy Selective Ion monitoring to confirm the identity of the analyte.

Method Validation

The minimum detection limit (MDL) criteria was determined by using the EPA technique based on multiple determinations of low concentrations of EDI, EDII, or EDS. The MDL was calculated to be 1.12 ng/mL for EDI, 3.62 ng/mL for EDII, and 3.7 ng/mL for EDS.

Collection and extraction efficiency was determined for a 50 ng spiked sample. The percent recovery was 101±1% for EDI, 81±3% for EDII, and 69±4% for EDS. The collection and extraction efficiency was also determined for a 150 ng spiked sample. The percent recovery was 90±1% for EDI, 71±1% for EDII, and 61±2% for EDS.

A sample storage stability study was conducted to determine the percent recovery for 50 ng of EDI, EDII, and EDS stored at 4° Celsius over a period of 20 days. The results of the stability study show EDI samples had a 103±1% recovery, EDII samples had a 89±3% recovery, and EDS samples had a 86±7% recovery over a period of 20 days. No breakthrough occurred during the 24 hours of dynamic sampling at 2 LPM air flow.

Documentation

All the samples received at the laboratory were accompanied by chain-of-custody records. Field data sheets containing the sample collection information were retained by ELB. The information recorded in the field data sheets included sampler ID, sampling date, start and stop times, flow rate, and comments about unusual conditions.

Laboratory and instrument maintenance logs were kept in bound notebooks with numbered pages. The entries made in the laboratory book included sample number, sample type, date sample was received, collection date, date of analysis, results of analysis, and analyst. The raw analytical data were recorded on electronic files and will be kept indefinitely by ELB.

VII. PERFORMANCE AUDITS

It should be noted that the percent difference for all Tables is calculated by using the following equation:

$$\frac{\text{Reported Value - True Value}}{\text{True Value}} \times 100$$

Flow Rate Audit

The flow rate for each sampler used was audited on July 17, 1996, following the procedures outlined in Attachment 2. The audit was conducted with a 0 to 3 LPM mass flow meter traceable to the National Institute of Standards and Technology (NIST). The difference between the reported and true flow rates for the ambient air samplers averaged 0.8% and ranged from -8.0% to 7.1% (Table 1).

Table 1
Results of the Flow Audit Conducted on the Ambient Samplers Used During the Monitoring for Endosulfan

Sampler Number	Reported Flow (LPM)	True Flow (LPM)	Percent Difference
6A	1.95	1.91	2.1
7A	1.95	1.89	3.2
12	1.95	1.84	6.0
13	1.95	1.82	7.1
20	1.95	2.12	-8.0
21	1.95	2.02	-3.5
22	1.95	1.96	-0.5
23	1.95	1.96	-0.5
24	1.95	1.92	1.6
25	1.95	1.94	0.5
26	1.95	1.95	0.0
27	1.95	1.91	2.1

Analytical Performance Audit

In August 1996, a total of 22 QA ambient audit samples were spiked with known amounts of QAS's standard solution of EDI, EDII, and EDS following the procedures outlined in Attachment 3. The 22 QA audit samples were designated as QA field spikes (5), QA trip spikes (10), and QA laboratory spikes (7). The QA field spikes were exposed to the same handling and storage conditions and also exposed to the same environmental and monitoring conditions as those occurring at the time of ambient sampling. The QA trip spikes followed the same handling and storage conditions of the ambient samples.

The seven QA laboratory spikes were stored at ELB's storage freezer for four days before extraction and analysis. The QA laboratory spikes were analyzed by ELB on August 30 and September 1, 1996. The audit results for EDI indicated a low recovery rate. The difference between the assigned and the reported total mass for EDI laboratory spikes averaged -74.1% with a range of -100% to -59.2% (Table 2).

The QAS staff, in conjunction with ELB, conducted an investigation to determine the cause of the low recovery results for EDI QA laboratory spikes. Staff was unable to find any inconsistencies with the sample solution, laboratory procedures, or spiking procedures. However, as part of the investigation it was noticed that the storage of the spiked standard solutions provided by AccuStandard and Axact is handled differently between the manufacturer's recommended

storing condition and the approved ELB Standard Operating Procedures (SOP). The manufacturer recommends the AccuStandard and Axact standard solutions to be stored at room temperature, whereas ELB's SOP recommends the solution. to be stored at 4° Celsius.

QAS staff contacted representatives from both the Axact and AccuStandards laboratories to determine what, if any, this change of temperature could have on the spiked samples. The representatives stated, at the initial concentrations given, a failure to allow the solutions to equilibrate to 20° Celsius before spiking could allow absorption of the EDI, EDII, or EDS concentration to the glass container. If the spiked solution did adhere to the container, poor results of the spiked samples would occur.

A second standard solution was prepared by ELB staff and compared to their working standard. This was prepared by ELB staff to determine the accuracy of their laboratory standard solution. In this comparison, ELB staff found no difference in standard solutions. It should be noted that in addition to this information, the laboratory standard concentration was created by using a pure or neat solution. This pure material is not dependant on temperature variations as is a diluted sample like the sample spiking solutions procured by AccuStandard and Axact. QA staff found no evidence to indicate the ambient results were affected by the temperature variations. Equilibration of the laboratory standards to room temperature was a standard operating practice in the analysis of all samples.

The QA laboratory spike audit results for EDII indicate a difference between the assigned and the reported total mass average of 4.6% with a range of -3.7% to 11.1%. For EDS, the audit results indicate a difference between the assigned and the reported total mass average of -28.7% with a range of -31.7 to -24.5% (Table 2). After review and discussion with ELB staff, it was determined that QA laboratory spike data for both EDII and EDS were reasonable.

Table 2
Results of Analyses of the QA Laboratory Spikes for Endosulfan I, Endosulfan II, and Endosulfan Sulfate

Sample ID	Assigned Mass (ng) EDI	EDII	EDS	Reported Mass (ng) EDI	EDII	EDS	% Difference EDI	EDII	EDS
AccuStandard									
QA-EL1	117.6	27	27.8	48	30	21	-59.2	11.1	-24.5
QA-EL2	117.6	27	27.8	45	29	20	-61.7	7.4	-28.1
QA-EL3	BLANK	BLANK	BLANK	ND	ND	ND	--	--	--
QA-EL4	8.4	BLANK	27.8	ND	ND	20	-100	--	-28.1
QA-EL5	8.4	BLANK	27.8	ND	ND	20	-100	--	-28.1
QA-EL6	42.0	27	27.8	16	26	19	-61.9	-3.7	-31.7
QA-EL7	42.0	27	27.8	16	28	19	-61.9	3.7	-31.7

The ten QA trip spikes were exposed to the same handling and storage conditions as those occurring at the time of ambient monitoring. The trip spikes were shipped, in an ice chest containing dry ice, from ELB laboratory to the Fresno ambient air monitoring station. At the Fresno site, the trip spikes were stored for four days in an ice chest containing dry ice, packaged with QA field spikes, and returned to ELB laboratory for analysis. The QA trip spikes were analyzed on two separate dates and used two separate standards: AccuStandard and Axact. The QA trip spiked samples identified as QA-ET1, QA-ET2, QA-ET3, QA-ET4, and QA-ET5 were analyzed by ELB on October 3-4, 1996, and used the standard solution from AccuStandard. The QA trip spiked samples identified as QA-ET6, QA-ET7, QA-ET8, QA-ET9, and QA-ET10 were analyzed by ELB on October 8-9, 1996, and used the standard solution from Axact.

The audit results for EDI indicated a low recovery rate using both the AccuStandard and Axact standard spikes. The difference for EDI between the assigned and the reported total mass for the five AccuStandard QA trip spikes averaged -94.9% with a range of -100% to -89.8% (Table 3). The difference between the assigned and the reported total mass for the five Axact QA trip spikes averaged -82.6% with a range of -100% to -64.3% (Table 3).

QAS staff, in conjunction with ELB, conducted an investigation to determine the cause of the low recovery results for EDI QA trip spikes. In December 1996, approximately three months after initial spiking, ELB staff conducted a "head-to-head" comparison for EDI, EDII, and EDS and analyzed the lab standard solution against the standard solutions used by QA staff provided by AccuStandard and Axact. This comparison found that the AccuStandard was comparable with the lab standard while the Axact standard recovery rate was low by a factor of 10. However, the

solutions used for spiking were stored differently for three months from the manufacture's recommended storing conditions before the head-to-head comparison was conducted. Axact Standards Inc. only guarantees their product if the temperature remains between 18 and 28° Celsius. Therefore, the head-to-head comparison does not provide a solution to the inconsistencies with the AccuStandard spikes. Based on the storage temperature issue noted above, it is a possibility that the Axact standard solution could have been compromised if the solution was not fully allowed to equilibrate to 20° Celsius before sampling.

Staff found no other inconsistencies with the sample solution, handling procedures, spiking procedures, and laboratory procedures other than the storage issue noted above. Based on the low recovery results for EDI QA trip spikes and the inconsistent sample storage procedures noted above, the impact on the ambient data cannot be determined at this time.

The QA trip spike audit results for EDII were complicated. The AccuStandard values reported non-detect for the samples spiked, therefore, these sample results were not reasonable. The Axact values indicate the difference between the assigned and the reported total mass of EDII averaged -27.8% with a range of -29.6% to -25.9% (Table 3). For EDS, all spikes were assigned blanks, and no contamination of the blanks were detected (Table 3). After review and discussion with ELB staff, it was determined that QA trip data for EDII Axact spikes and EDS trip blanks were reasonable.

Table 3
Results of Analyses of the QA Trip Spikes for
Endosulfan I, Endosulfan II, and Endosulfan Sulfate

Sample ID	Assigned Mass (ng)			Reported Mass (ng)			% Difference		
	EDI	EDII	EDS	EDI	EDII	EDS	EDI	EDII	EDS
AccuStandard									
QA-ET1	117.6	27	BLANK	12	ND	ND	-89.8	-100	--
QA-ET2	117.6	27	BLANK	12	ND	ND	-89.8	-100	--
QA-ET3	BLANK	BLANK	BLANK	ND	ND	ND	--	--	--
QA-ET4	8.4	BLANK	BLANK	ND	ND	ND	-100	--	--
QA-ET5	8.4	BLANK	BLANK	ND	ND	ND	-100	--	--
Axact Standard									
QA-ET6	117.6	27	BLANK	40	20	ND	-66.0	-25.9	--
QA-ET7	117.6	27	BLANK	42	19	ND	-64.3	-29.6	--
QA-ET8	BLANK	BLANK	BLANK	ND	ND	ND	--	--	--
QA-ET9	8.4	BLANK	BLANK	ND	ND	ND	-100	--	--
QA-ET10	8.4	BLANK	BLANK	ND	ND	ND	-100	--	--

The five QA field spikes were installed into the pesticide air monitor at this station and exposed to 24 hours of ambient air sampling through-the-tube samples at a rate of 2 LPM. A replicate air sampler (collocated) was used to collect and determine the background ambient air concentrations. After exposure to the field conditions, the samples were packaged, stored, and shipped in an ice chest containing dry ice to ELB for analysis.

The five QA field spikes audit samples were analyzed for EDI, EDII, and EDS. These samples were analyzed between October 8-9, 1996. The audit results for EDI indicated a low recovery rate. The difference between the assigned and the reported total mass for the EDI field spikes averaged -55.9% with a range of -61.7% to -46.4% (Table 4). Based on the low recovery results for EDI QA field spikes and the inconsistent sample storage procedures noted above, the impact on the ambient data cannot be determined at this time.

The QA field spike audit results indicate the difference between the assigned and the reported total mass for EDII averaged -16.7% with a range of -18.5% to -14.8% (Table 4). For EDS, all spikes were assigned blanks and no contamination was detected (Table 4). After review and discussion with ELB staff, it was determined that QA field spike data for both EDII and EDS were reasonable.

Table 4
Results of Analyses of the QA Field Spikes for
Endosulfan I, Endosulfan II, and Endosulfan Sulfate

Sample ID	Assigned Mass (ng)			Reported Mass (ng)			% Difference		
	EDI	EDII	EDS	EDI	EDII	EDS	EDI	EDII	EDS
AccuStandard									
QA-EF1	8.4	BLANK	BLANK	4.5	ND	ND	-46.4	--	--
QA-EF2	8.4	BLANK	BLANK	3.9	ND	ND	-53.6	--	--
QA-EF3	117.6	27	BLANK	45	23	ND	-61.7	-14.8	--
QA-EF4	117.6	27	BLANK	45	22	ND	-61.7	-18.5	--
QA-EF5	BLANK	BLANK	BLANK	ND	ND	ND	--	--	--

An investigation to determine the cause of the low recovery rates during QAS analytical performance audit for laboratory, trip, and field spikes of EDI was conducted by reviewing QA spiking standard solution handling, storage, and shipping records, along with records for analyses of QA spikes at ELB's laboratory. The following are the results of the investigation:

The QAS's endosulfan standards and ELB's endosulfan standards solutions were procured by AccuStandard Inc. and Axact Standards Inc. The standards had the same expiration date of September 1997. No spiking or calculation errors were found when reviewing QA spiking logbook.

The QAS endosulfan spiking solution procured from AccuStandard and Axact were analyzed by ELB on December 17, 1996, in a "head-to-head" comparison with the laboratory standard solution. ELB staff analyzed the results and found that the AccuStandard was comparable with the laboratory standard while the Axact standard measured rate was low by a factor of 10. However, the solutions used for spiking were stored differently for three months from the manufacture's recommended storing conditions before the head-to-head comparison was conducted. Axact Standards Inc. only guarantees their product if the temperature remains between 18 and 28° Celsius. Therefore, the head-to-head comparison does not provide a solution to the inconsistencies with the AccuStandard spikes.

A second standard solution was prepared by ELB staff and compared to their working standard. This was prepared by ELB staff to determine the accuracy of their laboratory standard solution. In this comparison, ELB staff found no difference in standard solutions. It should be noted that in addition to this information, the laboratory standard concentration was created by using a pure or neat solution. This pure material is not dependant on temperature variations as is a diluted sample like the sample spiking solutions procured by AccuStandard and Axact. QA staff found no evidence to indicate the ambient results were affected by the temperature variations. Equilibration of the laboratory standards to room temperature was a standard operating practice in the analysis of all samples.

The stability studies conducted by ELB staff determined that endosulfan was stable for 20 days when stored at 4° Celsius. The QA laboratory, trip, and field spiked samples were transported, stored, and analyzed within the 20-day stability requirement. No thermometer or recording of the temperature was logged during the storage of the spiked samples.

The Varian 3400 Gas Chromatograph was calibrated daily during the analysis of the ambient samples and QA spiked samples.

Review of the chromatograms and the sample analyses data showed no data transfer or calculation errors. Each spiked sample and ambient sample was analyzed using a single injection so no precision data could be established.

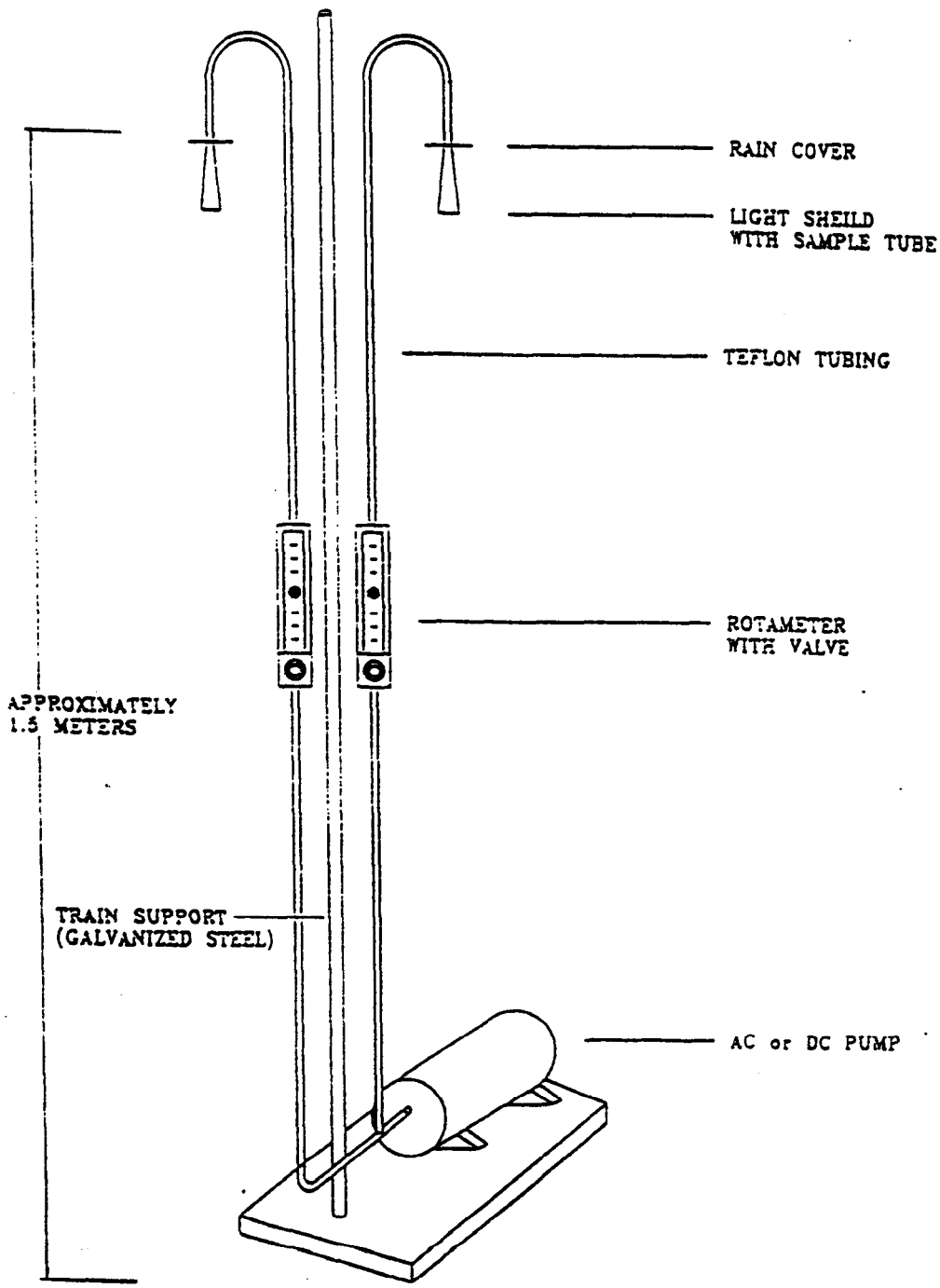
Storage of the standard solution is handled differently between the manufacturer's recommended storing condition and the approved ELB's SOP. The manufacturer recommends the standard solution be stored at room temperature in the dark, whereas ELB's SOP recommends the solution to be stored at 4° Celsius. However, if the standard solution is stored at the lower temperature, appropriate equilibration is needed to bring the standard solution to room temperature before use.

Representatives from both the Axact and AccuStandards laboratories were contacted to determine what, if any, this change of temperature could have on the samples of EDI. The representatives stated, at the initial concentrations of EDI given, a failure to allow the EDI solution to equilibrate to 20° Celsius before spiking could allow absorption of the EDI concentration to the glass container.

From the results of the investigation, the cause of the low recovery rates during QAS analytical performance audit for EDI field, trip, and laboratory spike samples could be caused by the temperature difference noted above. If the spiked solution did absorb to the container, poor results of the EDI spiked samples would occur. Based on the information provided, the impact on the ambient data compared with QAS spiking solution for EDI cannot be determined at this time.

ATTACHMENT 1

AIR SAMPLER USED IN MONITORING OF ENDOSULFAN



FLOW RATE AUDIT PROCEDURES FOR AIR SAMPLERS USED IN PESTICIDE MONITORING

Introduction

Air samplers are audited using a calibrated differential pressure gauge or a mass flow meter that is standardized against a National Institute of Standards and Technology (NIST) traceable flow calibrator. The audit device is connected in series with the sampler's flow meter. The flow rate is measured while the sampler is operating under normal sampling conditions. The sampler's indicated flow rate is corrected based on its calibration, and the true flow is calculated from the audit device's calibration curve. The sampler's reported flow is compared to the true flow, and a percent difference is determined.

Equipment

The basic equipment required for the air sampler flow audit is listed below. Additional equipment may be required depending on the particular configuration and type of sampler.

1. NIST-traceable mass flow meter.

2. Calibrated differential pressure gauge with laminar flow element.

3. 1/4" outer diameter Teflon tubing.

4. 1/4", stainless steel, Swagelock fittings.

Audit Procedures

1. If power is available, connect the mass flow meter into a 110 VAC outlet, and allow it to warm up for at least ten minutes. Otherwise, perform the audit with the calibrated differential pressure gauge.

2. Connect the inlet port of the audit device to the outlet port of the sampler's flow control valve with a five-foot section of Teflon tubing and Swagelock fittings.

3. Connect the outlet port of the audit device to the pump with another five-foot section of Teflon tubing and Swagelock fittings.

4. Allow the flow to stabilize for at least one to two minutes and record the flow rate indicated by the sampler and audit device's response.

5. Calculate the true flow rate from the audit device's response and record the results. Obtain the corrected sampler flow rate from the field operator. Calculate the percent difference between the true flow rate and the reported flow rate.

The percent difference is calculated by using the following equation:

$$\frac{\text{Reported Flow - True Flow}}{\text{True Flow}} \times 100$$

PERFORMANCE AUDIT PROCEDURES FOR THE LABORATORY ANALYSIS OF ENDOSULFAN I, ENDOSULFAN II, AND ENDOSULFAN SULFATE

Introduction

The purpose of the laboratory performance audit is to assess the accuracy of the analytical method used by the laboratory to measure the ambient concentrations of endosulfan I (EDI), endosulfan II (EDII), and the breakdown product endosulfan sulfate (EDS). The audit is conducted by submitting audit samples spiked with known concentrations of EDI, EDII, and EDS. The analytical laboratory reports the results to the Quality Assurance Section. The difference between the reported and the assigned concentrations is used as an indicator of the accuracy of the analytical method.

Materials

1. endosulfan I, 1.68 µg/mL endosulfan I in isooctane, AccuStandard Inc., Product #S-3346A, Lot #086-242, Expires 9/1/97.

2. endosulfan II, 5.4 µg/mL endosulfan II in isooctane, AccuStandard Inc., Product #S-3346B, Lot #086-243, Expires 9/1/97.

3. endosulfan sulfate, 5.55 µg/mL endosulfan sulfate in isooctane, AccuStandard Inc., Product #S-3346C, Lot #086-244, Expires 9/1/97.

4. endosulfan I, 1.68 µg/mL endosulfan I in isooctane, Axact Standards Inc., Catalog #13679, Lot #13679896, Expires 9/97.

5. endosulfan II, 5.4 µg/mL endosulfan II in isooctane, Axact Standards Inc., Catalog #13688, Lot #32090896, Expires 9/97.

6. endosulfan sulfate, 5.55 µg/mL endosulfan sulfate in isooctane, Axact Standards Inc., Catalog #13721, Lot #29550896, Expires 9/97.

7. XAD-2 adsorbent resin tubes, supplied by SKC West Inc.

Safety Precautions

Prior to handling any chemical, read the manufacturer's Material Safety Data Sheets (MSDS). Avoid direct physical contact with chemicals. Avoid breathing vapors. Use only under a fume hood. Wear rubber gloves, safety glasses, and protective clothing.

Preparation of Audit Samples

Prepare five field samples, ten trip samples, and seven laboratory audit samples by spiking the XAD-2 adsorbent cartridges with the volume of EDI, EDII, and EDS spiking solution indicated in Table 1 below. Using a microsyringe, insert the needle into the primary section of the XAD-2 cartridge, and push the plunger slowly while spiking the XAD-2 adsorbent resin.

Table 1
Volume of Endosulfan I, Endosulfan II, and Endosulfan Sulfate in Isooctane Used to Spike the QA Ambient Audit Samples

Sample ID	EDI Spiking Solution Volume (uL)	EDII Spiking Solution Volume (uL)	EDS Spiking Solution Volume (uL)
Field Spikes (AccuStandard's Standard Solutions)			
QA-EF1	5.0	0.0	0.0
QA-EF2	5.0	0.0	0.0
QA-EF3	70.0	5.0	0.0
QA-EF4	70.0	5.0	0.0
QA-EF5	0.0	0.0	0.0
Trip Spikes (AccuStandard's Standard Solutions)			
QA-ET1	70.0	5.0	0.0
QA-ET2	70.0	5.0	0.0
QA-ET3	0.0	0.0	0.0
QA-ET4	5.0	0.0	0.0
QA-ET5	5.0	0.0	0.0
Trip Spikes (Axact's Standard Solutions)			
QA-ET6	70.0	5.0	0.0
QA-ET7	70.0	5.0	0.0
QA-ET8	0.0	0.0	0.0
QA-ET9	5.0	0.0	0.0
QA-ET10	5.0	0.0	0.0
Laboratory Spikes (AccuStandard's Standard Solutions)			
QA-EL1	70.0	5.0	5.0
QA-EL2	70.0	5.0	5.0
QA-EL3	0.0	0.0	0.0
QA-EL4	5.0	0.0	5.0
QA-EL5	5.0	0.0	5.0
QA-EL6	25.0	5.0	5.0
QA-EL7	25.0	5.0	5.0

APPENDIX IV

PCA'S APPLICATION REPORT

TECKLENBURG RANCH
14860 N. WELLS LANE
LODI, CA 95240

APPLICATION SITE REPORT

From 01-01-97 to 04-08-97

-- MATERIAL ---	COMPLETE DATE	TREATED - ACRE-	APPLIED -- RATE/ACRE	--- TOTAL --- MATR. APPL	DILUT. VOLUME	----- APPLICATION ---- REASON --------	APPLI. METHOD	TOTAL COST $20.	AVERAGE COST $20./A
TECKLENBURG 1-1	Crop : APPLE		Harvest: 10-15-96			Total Area: 8.50 ACRE			
GLYPHOS	01-31-97	8.50	2.00 QT	4.25 GAL	40.00	WEEDS	GROUND	216.75	120.62
GOAL 2X	11:00	#69	2.00 QT	4.25 GAL		APP: TECKLENBURG		442.00	
SIM-TROL 90DF			1.00 LB	8.50 LB				35.70	
SURFLAN AS			2.00 QT	4.25 GAL				330.86	
SUPERCIDE WP	02-27-97	10.00	4.00 LB	40.00 LB	200.00	APHID	GROUND	640.00	98.24
SUPER 94 OIL	08:00	#74	6.00 GAL	60.00 GAL		APP: TECKLENBURG		195.00	
AGRA-MYCIN 17	03-10-97	8.50	8.00 OZ	68.00 OZ	100.00	FIREBLIGHT	GROUND	138.04	45.49
PROCURE 50WS	09:00	#76	8.00 OZ	4.25 LB		APP: TECKLENBURG		248.63	
THIODAN 50WP	04-08-97	6.00	3.00 LB	18.00 LB	100.00	WORMS & FIRE BLIGHT, S	GROUND	129.60	36.57
AGRA-MYCIN 17	07:45	#84	8.00 OZ	48.00 OZ		APP: TECKLENBURG		97.44	
THIRAM WP			3.00 LB	18.00 LB				36.00	
9-18-9			1.00 GAL	6.00 GAL				27.00	
SYMSPRAY			12.00 OZ	0.56 GAL				20.81	
TOTAL--------	4	33.00	APPLE				COST	2557.83	300.92
-------YIELD---	AVERAGE:25.00 BUSHELS/ACRE			TOTAL:212.50 BUSHELS			INCOME	5312.50	625.00
----------							DIFFER	2754.67	324.08
GRAND TOTAL--	4	33.00					COST	2557.83	300.92
----------							INCOME	5312.50	625.00
----------							DIFFER	2754.67	324.08

APPENDIX V

DPR'S MONITORING RECOMMENDATION

State of California

Memorandum

To George Lew, Chief
Engineering and Laboratory Branch
Monitoring and Laboratory Division
Air Resources Board
600 North Market Boulevard
Sacramento, California 95812

Date March 20, 1996

Place

From **Department of Pesticide Regulation** — 1020 N Street, Room 161
Sacramento, California 95814-5624

Subject MONITORING RECOMMENDATION FOR ENDOSULFAN

Attached is the Department of Pesticide Regulation's recommendation for monitoring the herbicide endosulfan. This recommendation is provided pursuant to the requirements of AB 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5). As you know, monitoring recommendations are made using historical use information for the pesticide in question. For this reason, it is essential that the agricultural commissioner, in the county or counties where monitoring will be conducted, be consulted prior to the onset of air monitoring.

We anticipate submission of air monitoring data by October 1997.

If you have any questions please contact Kevin Kelley, of my staff, at (916) 324-4187.

John S. Sanders, Chief
Environmental Monitoring and Pest Management Branch
(916) 324-4100

cc: Paul H. Gosselin, DPR
Charles M. Andrews, DPR
Ronald J. Oshima, DPR
Gary Patterson, DPR
Barry Cortez, DPR
John Donahue, DPR
Kevin Kelley, DPR
Madeline Brattesani, DPR
Genevieve Shiroma, ARB
Ruth Tomlin, ARB
Cara Roderick, ARB

Cosmo C. Insalaco, Fresno County Agricultural Commissioner
Mark Lockhart, Lake County Agricultural Commissioner
Erwin B. Elby, San Joaquin County Agricultural Commissioner

SURNAME			

Staff Report

USE INFORMATION AND AIR MONITORING RECOMMENDATION FOR THE PESTICIDAL ACTIVE INGREDIENT ENDOSULFAN

March 1996

Principal Author

Kevin C. Kelley

Associate Environmental Research Scientist

MONITORING RECOMMENDATION FOR ENDOSULFAN

To fulfill the requirements of AB 1807/3219 (California Food and Agricultural Code, Division 7, Chapter 3, Article 1.5), the Department of Pesticide Regulation (DPR) has previously requested that the Air Resources Board (ARB) document the airborne concentrations of the pesticide endosulfan [(3α,5aβ,6α,9α,9aβ)- or (3α,5aα,6β,9β,9aα)-6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide]. This recommendation provides background and recent use information on endosulfan containing products, and identifies how they are used.

The technical grades of endosulfan are mixtures of two stereoisomers α-Endosulfan (64-67%) and β-endosulfan (32-29%) with approximately 4% other material. α-Endosulfan [(3α,5aβ,6α,9α,9aβ)-6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide] (CAS: 959-98-8) and β-endosulfan [(3α,5aα,6β,9β,9aα)-6,7,8,9,10,10-Hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo-dioxathiepin-3-oxide] (CAS:33213-65-9) are colorless to brown crystals emitting a sulfur dioxide-like odor. Endosulfan has a molecular formula of $C_9H_6Cl_6O_3S$, a formula weight of 460.92 g/mole and a specific density of 1.745 at 20 °C. Endosulfan has a vapor pressure of 10^{-5} mmHg at 25 °C, but water solubility (S_w), and Henry's Constant (K_H) vary with isomer. α-Endosulfan S_w = 530 ppb at 25 °C, K_H = 1.01 x 10^{-4} atm·m³/mol at 25 °C, β-endosulfan S_w = 280 ppb at 25 °C, K_H = 1.91 x 10^{-5} atm·m³/mol at 25 °C. Both isomers are soluble in most organic solvents.

The hydrolysis half-life ($t_{1/2}$) of endosulfan in water (25 °C and pH 7) is 218 hours for α-endosulfan and 187 hours for β-endosulfan. In plants the $t_{1/2}$ for conversion of α-Endosulfan to β-endosulfan is approximately 60 days, and the $t_{1/2}$ for the conversion of β-endosulfan to endosulfan sulfate is 800 days. Each isomer forms its respective sulfate on exposure to light in surface waters.

Degradation of endosulfan in soil yields a mixture of endosulfandiol, endosulfanhydroxy ether, endosulfan lactone and endosulfan sulfate. Endosulfan sulfate is the major biodegradation product in soils under aerobic, anaerobic and flooded conditions. In flooded soils, endosulfandiol and endohydroxy ether were also reported. In sandy loam soil, microorganisms are responsible for degrading endosulfan to endosulfandiol, and further to endosulfan α-hydroxy ether and trace amounts of endosulfan ether. Both products are subsequently converted to endosulfan lactone. This soil transformation pathway is followed by both isomeric forms.

The acute oral LD_{50} of endosulfan for rats is 70 mg/kg (aqueous), and 110 mg/kg in oil. Acute LC_{50} (1-hour) for rats > 21 mg/L air. Acute dermal LD_{50} is 500 mg/kg for rats and 369 mg/kg for rabbits. The LC_{50} (96 hour) irrespective of isomer are 0.3 µg/L for rainbow trout, and 3.0 µg/L for white sucker. Endosulfan has entered the risk assessment process at DPR under the SB 950 (Birth Defect Prevention Act of 1984) based on its potential reproductive and neurotoxicity adverse health effects.

As of March 8, 1995, there were 19 active registrations for products containing endosulfan. Eighteen are agricultural products and one is a home-garden product. Formulations of endosulfan include granulars, emulsifiable concentrates and wettable powders. Technical endosulfan is formulated as a dust. The Signal Words on agricultural endosulfan-containing products are "Danger: or "Danger/Poison", and "Warning" on the home garden (9.15% AI) product.

Use of endosulfan for 1993, 1992 and 1991 is summarized in the following tables: Table 1, endosulfan use by year; and Table 2, endosulfan applications in Fresno County. Agricultural use of endosulfan for the eleven counties listed in Table 1 accounts for 92% to 97% of total endosulfan use. Remaining use is for the treatment of containerized plants and flowers in greenhouses and nurseries.

Table 1: Endosulfan Use by Year.
(Pounds of Active Ingredient)

County	1993	1992	1991
Fresno	116,248.76	150,302.29	64,431.70
Imperial	45,847.24	56,700.93	143,111.70
Kern	74,771.36	63,086.13	35,941.01
Kings	27,243.66	9,371.94	4,407.76
Lake	1,435.33	2,183.34	4,065.62
Madera	3,993.57	6,080.14	11,017.66
Riverside	24,250.59	32,096.95	22,405.34
San Joaquin	3,191.48	6,944.20	4,385.12
Stanislaus	1,651.88	2,549.94	2,281.04
Sutter	4,545.89	8,589.03	2,758.43
Tulare	52,385.36	30,765.79	17,480.53
County Totals	355,565.13	368,670.68	312,285.91
TOTAL CA USE	366,008.3	383,006.7	339,581.3

The Pesticide Use Report (PUR) data summarized in Table 1 show that the largest applications of endosulfan generally occur in Fresno County. Although applications in Imperial County in 1991 were 2+ times greater those of Fresno County, this use probably was the result of the silver-leaf whitefly infestation which occurred there during the summer of that year. Additionally, PUR data indicates that the greatest applications generally begin in May and June peaking in either July or August depending on year (Table 2).

Table 2. Endosulfan applications in Fresno County
(Pounds of Active Ingredient)

Fresno County	1993	1992	1991
May (lbs AI)	3,698.27	23,759.96	4,050.94
(Rate)	0.94	1.21	1.17
June (lbs AI)	13,186.77	19,424.16	18,349.19
(Rate)	0.89	0.99	1.06
July (lbs AI)	22,304.57	58,865.88	18,074.12
(Rate)	1.00	1.37	1.01
August (lbs AI)	59,528.64	15,598.53	7,935.87
(Rate)	1.00	0.90	0.99

RECOMMENDATIONS:

Ambient Air Monitoring.

The use patterns for endosulfan suggests that monitoring should take place in Fresno County during a 30- to 45-day sampling period in the months of July and August. Three to five sampling sites should be selected in relatively high-population areas or in areas frequented by people. Sampling sites should be in cotton or grape growing areas but not immediately adjacent to fields to which endosulfan is being applied. At each site, twenty to thirty discrete 24-hour samples should be taken during the sampling period. Background samples should be collected in an area distant to endosulfan applications.

Replicate (CO-located) samples are needed for five dates at each sampling location. Two co-located samplers (in addition to the primary sampler) should be run on those days. The date chosen for replicate samples should be distributed over the entire sampling period. They may, but need not be, the same dates at every site. Field blank and spike samples should be collected at the same environmental (temperature, humidity, exposure to sunlight) and experimental (air flow rates) conditions as those occurring at the time of ambient sampling. Since endosulfan is known to partition into fogwater, samples collected during fog episodes should be designated as such.

Monitoring of an Application Site.

There is no specific use pattern for endosulfan where the application rate is greater than 1.5 lbs AI/acre. PUR Use data (1991 through 1993) indicates that endosulfan applications to grapes (wine and fresh market) in Fresno and Kern counties routinely occurs from May through August but use rates rarely exceed 1.5 lbs AI/acre. Applications of endosulfan in Lake County to pears regularly exceeds 2.0 lbs AI/acre during September and October. Applications

to cherries or apples in San Joaquin County during April exceeds 2.25 lbs AI/acre; Applications to nectarines in Fresno County also in April exceeds 2.1 lbs AI/acre.

Use patterns for endosulfan suggests that application-site monitoring should be conducted during the months of September or October in Lake County, and that the application be associated with pears. Alternatively, monitoring may be performed in San Joaquin County in April (applications associated with cherries or apples) or in Fresno County during April (applications associated with almonds. Although endosulfan is not used extensively on these crops during this period, care should still be taken so that other applications to nearby groves during the sampling period do not affect sample collection. A three day monitoring period should be established with sampling times as follows. Application + 1 hour, followed by one 2-hour sample, one 4-hour sample, two 8-hour samples and two 24-hour samples. A minimum of four samplers should be positioned, one on each side of the field. A fifth sampler should be co-located at one position. Since endosulfan is extensively used in the area, background samples should collect enough volume (either 12 hours at 15 liters/min., or a shorter period with a higher volume pump) to permit a reasonable minimum detection level. Ideally, samplers should be placed a minimum of 20 meters from the field. Field blank and field spike samples should be collected at the same environmental (temperature humidity, exposure to sunlight) and experimental (similar air flow rates) conditions as those occurring at the time of sampling.

We also request that you provide in the monitoring report: 1) An accurate record of the positions of the monitoring equipment with respect to the field (please include the exact distance that the sampler is positioned from the field), 2) an accurate drawing of the monitoring site showing the precise location of the meteorological equipment, trees, buildings, and other obstacles, 3) meteorological data collected at a minimum of 15 minute intervals including wind speed and direction, humidity, and comments regarding degree of cloud cover, and 4) the elevation of each sampling station with respect to the field, and the orientation of the field with respect to North (identified as either true or magnetic North). Samples collected during fog episodes should be designated as such.

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APPENDIX VI

APPLICATION AND AMBIENT FIELD LOG SHEETS FOR ENDOSULFAN

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
1	1CC	7-29 7-30	1205 0950	R. To 12	K	B.T.
2	1WE	7-29 7-30	1244 1020	R. To 24	K	
3	1SJ	7-29 7-30	1125 0915	R. To 26	K	
4	1TQ	7-29 7-30	1140 0930	R. To 23	K	
5	1ARB	7-29 7-30	1400 0820	R. To 20	K	
6	2CC	7-30 7-31	0950 1005	R. To 12	K	
7	2WE	7-30 7-31	1020 1030	R. To 24		
8	2SJ	7-30 7-31	0915 0920	R. To 26		
9	2TQ	7-30 7-31	0930 0945	R. To 23		
10	2ARB	7-30 7-31	0820 0830	R. To 20		
11	3CC	7-31 8-1	1005 1000	R. To 12		
12	3CC-D	7-31 8-1	1005 1000	R. To 13		
13	3WE	7-31 8-1	1030 1035	R. To 24		
14	3WE-D	7-31 8-1	1030 1035	R. To 25		
15	3SJ	7-31 8-1	0920 0915	R. To 26		
16	3SJ-D	7-31 8-1	0920 0915	R. To 27		
17	3TQ	7-31 8-1	0945 0935	R. To 23		
18	3TQ-D	7-31 8-1	0945 0935	R. To 22		
19	3ARB	7-31 8-1	0830 0830	R. To 20		
20	3ARB-D	7-31 8-1	0830 0830	R. To 21		
21	4CC	8-1 8-2	1000 1000	R. To 12		
22	4WE	8-1 8-2	1035 1025	R. To 24	↓	↓

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
23	4SJ	8-1	0915	R, T6 26	K	LDT
		8-2	0920			
24	4TQ	8-1	0935	R, T5 23		
		8-2	0935			
25	4ARB	8-1	0830	R, T6 20		
		8-2	0830			
26	Blank	8-2	1030			
27	5CC	8-5	1250	ROTO 12	K	LJT
		8-6	1055			
28	5WE	8-5	1310	ROTO 24		
		8-6	1120			
29	5SJ	8-5	1200	ROTO 26		
		8-6	1010			
30	5TQ	8-5	1225	ROTO 22		
		8-6	1030			
31	5ARB	8-5	~~1460~~	ROTO 20		
		8-6	0840			
32	6CC	8-6	1055	ROTO12		
		8-7	1045			
33	6WE	8-6	1120	ROTO 24		
		8-7	1115			
34	6SJ	8-6	1010	ROTO 26		
		8-7	1000			
35	6TQ	8-6	1030	ROTO 22		
		8-7	1020			
36	6ARB	8-6	0840	ROTO 20		
		8-7	0840			
37	7CC	8-7	1045	ROTO 12		
		8-8	0955			
38	7CC-D	8-7	1045	ROTO13		
		8-8	0955			
39	7WE	8-7	1115	ROTO 24		
		8-8	1025			
40	7WE-D	8-7	1115	ROTO 25		
		8-8	1025			
41	7SJ	8-7	1000	ROTO 26		
		8-8	0915			
42	7SJ-D	8-7	1000	ROTO 27		
		8-8	0915			
43	7TQ	8-7	1020	ROTO 22		
		8-8	0930			
44	7TQ-D	8-7	1020	ROTO 23		
		8-8	0930			

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear | taken by	
45	7ARB	8-7 8-8	0840 0800	ROTO 20	K	LJT
46	7AEB-D	8-7 8-8	0840 0800	ROTO 21		
47	8CC	8-8 8-9	0955 0920	ROTO 12		
48	8WE	8-8 8-9	025 0940	ROTO 24		
49	8SJ	8-8 8-9	0915 0845	ROTO 26		
50	8TQ	8-8 8-9	0930 0855	ROTO 22		
51	8ARB	8-8 8-9	0800 0730	ROTO 20		
52	Blank	8-9	0945	TAKEN AT WE SITE	↓	↓
53	9CC	8-12 8-13	1030 1005	Roto 12	K hot	B.T.
54	9WE	8-12 8-13	1200 1035	Roto 24		
55	9SJ	8-12 8-13	1115 0930	Roto 26		
56	9TQ	8-12 8-13	1100 0940	Roto 22		
57	9ARB	8-12 8-13	1300 0840	Roto 20		
58	10CC	8-13 8-14	1005 0950			
59	10WE	8-13 8-14	1035 1015			
60	10SJ	8-13 8-14	0930 0915			
61	10TQ	8-13 8-14	0940 0930			
62	10ARB	8-13 8-14	0840 0830			
63	11CC	8-14 8-15	0950 0950			
64	11CC-D	8-14 8-15	0950 0950	Roto 13		
65	11WE	8-14 8-15	1015 1020			
66	11WE-D	8-14 8-15	1015 1030	Roto 25	↓	↓

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
67	11SJ	8-14 8-15	0915 0915		K - hot	B.T.
68	11SJ-D	8-14 8-15	0915 0915	RoTo 27		
69	11TQ	8-14 8-15	0930 0930			
70	11TQD	8-14 8-15	0930 0930	RoTo 23		
71	11ARB	8-14 8-15	0830 0830			
72	11ARB-D	8-14 8-15	0830 0830	RoTo 31		
73	BLNK	8-15	1020	West End Site		
74	12CC	8-15 8-16	0950 0950			
75	12WE	8-15 8-16	1020 1020			
76	12SJ	8-15 8-16	0915 0915			
77	12TQ	8-15 8-16	0930 0930			
78	12ARB	8-15 8-16	0830 0830			
79	13CC	8-19 8-20	1205 1055	ROTO 12	K	d.J.
80	13WE	8-19 8-20	1230 1120	ROTO 24		
81	13SJ	8-19 8-20	1130 1010	ROTO 26		
82	13TQ	8-19 8-20	1145 1035	ROTO 22		
83	13ARB	8-19 8-20	1345 0900	ROTO 20		
84	14CC	8-20 8-21	1055 1055			
85	14WE	8-20 8-21	1120 1120			
86	14SJ	8-20 8-21	1010 0955			
87	14TQ	8-20 8-21	1035 1020			
88	14ARB	8-20 8-21	0900 0835			

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
89	15CC	8-21 8-22	1055 1020	ROTO 12	K	L.J.
90	15CC-D	8-21 8-22	1055 1020	ROTO 13		
91	15WE	8-21 8-22	1120 1100	ROTO 24		
92	15WE-D	8-21 8-22	1120 1100	ROTO 25		
93	15SJ	8-21 8-22	2955 0940	ROTO 26		
94	15SJ-D	8-21 8-22	0955 0940	ROTO 27		
95	15TQ	8-21 8-22	1020 1000	ROTO 22		
96	15TQ-D	8-21 8-22	1020 1000	ROTO 23		
97	15ARB	8-21 8-22	0835 0830			
98	15ARB-D	8-21 8-22	0835 0830			
99	16CC	8-22 8-23	1020 0925			
100	16WE	8-22 8-23	1100 0950			
101	16SJ	8-22 8-23	0940 0850			
102	16TQ	8-22 8-23	1000 0905			
103	16ARB	8-22 8-23	0830 0730			
104	BLANK	8-23	0730	TAKEN AT ARB SITE		
105	17CC	8-26 8-27	1250 1025	ROTO 12		
106	17WE	8-26 8-27	1315 1050	ROTO 24		
107	17SJ	8-26 8-27	1200 0950	ROTO 26		
108	17TQ	8-26 8-27	1230 1000	ROTO 22		
109	17ARB	8-26 8-27	1400 0835	ROTO 20		
110	18CC	8-27 8-28	1025 1025			

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
111	18NE	8-27	1050		K	D.J.
		8-28	1055			
112	18SJ	8-27	0950			
		8-28	0935			
113	18TQ	8-27	1000			
		8-28	0955			
114	18ARB	8-27	1035			
		8-28	1030			
115	19CC	8-28	1025			
		8-29	1100	ROTO 12		
116	19CC-D	8-28	1025			
		8-29	1100	ROTO 13		
117	19NE	8-28	1055			
		8-29	1135	ROTO 24		
118	19NE-D	8-28	1055			
		8-29	1135	ROTO 25		
119	19SJ	8-28	0935			
		8-29	1005	ROTO 26		
120	19SJ-D	8-28	0935			
		8-29	1005	ROTO 27		
121	19TQ	8-28	0955			
		8-29	1040	ROTO 22		
122	19TQ-D	8-28	0955			
		8-29	1040	ROTO 23		
123	19ARB	8-28	1230			
		8-29	0840	ROTO 20		
124	19ARB-D	8-28	1230			
		8-29	0840	ROTO 21		
125	20CC	8-29	1100			
		8-30	0955			
126	20NE	8-29	1135			
		8-30	1030			
127	20SJ	8-29	1005			
		8-30	0915			
128	20TQ	8-29	1040			
		8-30	0930			
129	20ARB	8-29	0840			
		8-30	0740			
130	BLANK	8-30	0740	TAKEN AT ARB SITE		
131	QAEF1	8-28	1230	FIELD SPIKE ROTO 6A ARB SITE		
		8-29	0840			
132	QAEF2	8-28	1230	FIELD SPIKE ROTO 7A ARB SITE DUPLICATE		
		8-29	0840			

LOG BOOK
Project: Endosulfan Ambient
Project #: C96-034

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
133	QAEF3	8-29 8-30	0840 0740	FIELD SPIKE ROTO 6A ARB SITE	K	J.J.
134	QAEF4	8-29 8-30	0840 0740	" " ROTO 7A DUPICATE		
135	QAEF5	8-29 8-30	0840 0740	" " ROTO 21 TRIPLICATE		
136	QAET1	8-28	—	TRIP SPIKE		
137	QAET2	8-28	—			
138	QAET3	8-28	—			
139	QAET4	8-28	—			
140	QAET5	8-28	—			
141	QAET6	8-28	—			
142	QAET7	8-28	—			
143	QAET8	8-28	—			
144	QAET9	8-28	—			
145	QAET10	8-28	—			

2 l/min

LOG BOOK
Project: Endosulfan Application
Project #: C97-004

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
1	ENDEB	4/4/96	1325	ROTO	K	KEM
		4/5/96	1050			
2	EFS1	4/4/96	1325			
		4/5/96	~~1355~~	1050		
3	NB	4/4/96	1330			
		4/5/96	1045	12A		
4	NFS2	4/4/96	1330			
		4/5/96	1045	12B		
5	WB	4/4/96	1350			
		4/5/96	1040	9A		
6	WFS3	4/4/96	1350			
		4/5/96	1040	9B		
7	SB	4/4/96	1405			
		4/5/96	1055	8A		
8	SFS4	4/4/96	1405			
		4/5/96	1055	8B		
9	QATS 1			Trip Spikes		
10	2			"		
11	3			"		
12	4			"		
13	ENDEB2	4/7/97	1705	Background	K	KEM
		4/8	0530			
14	SB2	4/7/97	1710			
		4/8	0525			
15	WB2	4/7/97	1715			
		4/8	0515			
16	NB2	4/7/97	1725	9A		
		4/8	0540			
17	ENDW1	4/8	0515			
		4/8	0845			
18	S1	4/8/97	0520			
		4/8	0850			
19	S10	4/8	0520			
		4/8	0850	Dup		
20	E1	4/8	0530			
		4/8	0855			
21	N1	4/8	0540	(9A)		
		4/8	0900			

Start @ 0545

LOG BOOK
Project: Endosulfan Application
Project #: C97-004

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
22	ENDW2	4/5	0945		K	KEM
		4/8	1040			
23	S2	4/8	0950			
		4/8	1045			
24	S2D	4/8	0950			
		4/8	1045			
25	E2	4/8	0955			
		4/8	1045			
26	N2	4/8	0900	9B		NVA
		4/8	1050			
27	ENDW3	4/5	1040			
		4/8	1440			
28	S3	4/8	1045			
		4/8	1445	10A		
29	S3D	4/5	1045			
		4/8	1445	10B		
30	E3	4/5	1045			
		4/8	1450			
31	N3	4/5	1050			
		4/8	1455			
32	ENDW4	4/5	1445	12A		
		4/8	2245			
33	S4	4/8	1445	10A		
		4/8	2250			
34	S4D	4/8	1445	10B		
		4/8	2250			
35	E4	4/8	1450	8B		
		4/8	2255			
36	N4	4/8	1455	9B		
		4/8	2300			
37	ENDW5	4/8	2245			
		4/9	0815			
38	S5	4/8	2250			
		4/9	0820			
39	S5D	4/8	2250			
		4/9	0820			
40	E5	4/8	2255			
		4/9	0825			
41	N5	4/8	2300			
		4/9	0830			
42	ENDW6	4/9	0815			
		4/10	0800			
43	S6	4/9	0820			
		4/10	0805			

LOG BOOK
Project: Endosulfan Application
Project #: C97-004

Log Number	Sample ID	Date	Time	Comments	weather o = overcast pc = partly cloudy k = clear	taken by
44	SGD	4/9	0820			
		4/10	0805			
45	E6	4/9	0825			
		4/10	0810			
46	N6	4/9	0830			
		4/10	0815			
47	ENDS	4/10	0800			
		4/11	0800			
48	S7	4/10	0805			
		4/11	0805			
49	S7D	4/10	0805			
		4/11	0805			
50	E7	4/10	0810			
		4/11	0810			
51	N7	4/10	0815			
		4/11	0815			

APPENDIX VII

ENDOSULFAN APPLICATION METEOROLOGICAL DATA

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	97	1803	0.38	72.0	1015.0	37.1	256
1997	97	1818	1.91	70.6	1015.0	42.2	289
1997	97	1833	5.94	69.5	1015.0	45.3	271
1997	97	1848	9.26	68.3	1015.0	45.9	266
1997	97	1903	9.87	66.8	1015.0	43.7	274
1997	97	1918	11.11	64.4	1015.0	52.0	273
1997	97	1933	9.65	63.2	1015.0	52.4	275
1997	97	1948	9.64	62.0	1015.0	57.8	268
1997	97	2003	11.10	60.9	1015.0	56.8	258
1997	97	2018	7.92	60.1	1015.7	57.8	258
1997	97	2033	8.25	59.7	1015.9	59.4	250
1997	97	2048	7.17	59.4	1016.0	58.3	249
1997	97	2103	6.86	59.0	1016.0	57.6	254
1997	97	2118	4.43	58.6	1016.0	58.0	251
1997	97	2133	2.99	58.1	1016.0	60.1	254
1997	97	2148	0.73	57.4	1016.0	63.1	254
1997	97	2203	3.95	57.1	1016.0	65.4	261
1997	97	2218	4.39	57.4	1016.0	64.1	264
1997	97	2233	2.88	57.5	1016.0	61.8	232
1997	97	2248	0.50	55.8	1016.0	67.2	234
1997	97	2303	0.00	55.7	1016.0	66.2	211
1997	97	2318	2.02	56.3	1016.0	63.8	252
1997	97	2333	1.29	56.2	1016.0	62.7	261
1997	97	2348	0.00	55.3	1016.0	65.2	142
1997	98	0003	0.00	54.6	1016.0	67.1	182
1997	98	0018	0.00	53.7	1016.0	68.2	204
1997	98	0033	0.07	53.8	1016.0	66.2	297
1997	98	0048	0.03	53.5	1016.0	66.6	281
1997	98	0103	0.00	53.1	1015.5	66.3	288
1997	98	0118	0.00	51.5	1015.0	69.4	262
1997	98	0133	0.00	51.3	1015.5	71.9	316
1997	98	0148	0.00	50.0	1015.5	75.2	293
1997	98	0203	0.00	49.7	1015.0	75.1	323
1997	98	0218	0.00	51.0	1015.0	73.7	306
1997	98	0233	0.00	49.0	1015.0	77.4	347
1997	98	0248	0.00	48.2	1015.0	79.0	241
1997	98	0303	0.00	47.0	1014.5	79.7	97
1997	98	0318	0.00	46.6	1014.7	81.7	249
1997	98	0333	0.00	46.3	1014.0	87.1	64
1997	98	0348	0.00	46.2	1014.0	86.7	135
1997	98	0403	0.00	47.5	1014.0	84.1	242
1997	98	0418	0.00	45.9	1014.0	86.9	133
1997	98	0433	0.00	44.3	1014.0	87.2	112
1997	98	0448	0.00	44.3	1014.0	87.3	89
1997	98	0503	0.00	44.5	1014.0	87.3	87

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	98	0518	0.13	44.2	1014.0	88.3	120
1997	98	0533	0.00	43.7	1014.0	89.9	87
1997	98	0548	0.00	42.7	1014.0	95.4	253
1997	98	0603	0.00	42.2	1014.0	95.4	156
1997	98	0618	0.00	41.8	1014.7	95.8	176
1997	98	0633	0.00	41.3	1015.0	95.3	164
1997	98	0648	0.00	40.7	1015.0	98.4	144
1997	98	0703	0.00	41.1	1015.0	99.1	81
1997	98	0718	0.00	42.2	1015.0	98.1	124
1997	98	0733	0.00	44.2	1015.0	96.8	139
1997	98	0748	0.00	49.4	1015.0	94.6	139
1997	98	0803	0.02	50.4	1015.0	89.7	220
1997	98	0818	4.63	52.6	1015.0	83.0	268
1997	98	0833	5.56	53.7	1015.3	78.2	271
1997	98	0848	6.65	54.6	1015.0	76.6	274
1997	98	0903	7.10	55.4	1015.0	75.4	271
1997	98	0918	6.05	56.7	1015.0	71.2	272
1997	98	0933	5.17	58.3	1015.0	69.3	260
1997	98	0948	4.65	59.4	1015.0	64.6	276
1997	98	1003	3.61	60.7	1015.0	62.6	277
1997	98	1018	3.70	62.1	1015.0	58.9	271
1997	98	1033	5.51	62.2	1015.0	60.8	265
1997	98	1048	4.35	62.3	1015.0	62.1	277
1997	98	1103	1.84	63.4	1015.0	63.6	285
1997	98	1118	1.68	63.7	1015.0	63.0	277
1997	98	1133	1.74	64.1	1015.0	56.1	261
1997	98	1148	0.58	64.7	1015.0	54.1	286
1997	98	1203	1.36	65.0	1015.0	55.3	289
1997	98	1218	0.87	65.9	1015.0	53.7	267
1997	98	1233	1.81	66.7	1015.0	52.2	270
1997	98	1248	1.91	67.7	1015.0	51.3	262
1997	98	1303	1.77	67.5	1014.5	49.2	272
1997	98	1318	0.40	68.4	1014.0	46.9	273
1997	98	1333	0.13	69.9	1014.0	43.6	281
1997	98	1348	0.01	70.7	1014.0	42.1	252
1997	98	1403	0.00	70.7	1014.0	40.7	276
1997	98	1418	0.00	70.9	1014.0	40.3	282
1997	98	1433	0.00	71.9	1013.1	40.8	269
1997	98	1448	0.42	71.9	1013.0	38.5	272
1997	98	1503	1.15	71.8	1013.0	39.8	260
1997	98	1518	4.47	71.6	1013.0	39.0	254
1997	98	1533	3.14	71.5	1013.0	37.8	259
1997	98	1548	2.40	71.8	1013.0	36.7	257
1997	98	1603	5.43	71.6	1012.6	34.7	250
1997	98	1618	6.73	71.4	1012.0	33.0	278
1997	98	1633	11.15	71.5	1012.0	31.1	271

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	98	1648	14.56	70.6	1012.0	28.3	264
1997	98	1703	14.40	69.9	1012.0	33.4	271
1997	98	1718	15.49	69.0	1012.0	33.3	263
1997	98	1733	16.35	67.9	1012.0	33.9	260
1997	98	1748	16.48	66.8	1012.0	28.1	261
1997	98	1803	16.94	66.0	1012.0	29.8	256
1997	98	1818	17.03	65.2	1012.0	33.4	254
1997	98	1833	15.32	64.7	1012.0	34.1	255
1997	98	1848	16.69	63.7	1012.0	32.9	257
1997	98	1903	12.95	62.9	1012.0	37.0	257
1997	98	1918	13.50	61.9	1012.0	38.6	256
1997	98	1933	12.88	60.6	1011.4	43.4	254
1997	98	1948	8.96	59.8	1011.0	45.1	251
1997	98	2003	8.94	59.3	1011.3	46.3	256
1997	98	2018	9.06	58.9	1012.0	49.3	245
1997	98	2033	14.95	58.4	1012.0	49.9	258
1997	98	2048	11.00	57.0	1012.0	54.6	248
1997	98	2103	10.48	56.2	1012.1	56.9	267
1997	98	2118	14.18	55.3	1012.7	59.1	258
1997	98	2133	18.11	54.6	1012.7	60.7	253
1997	98	2148	15.66	53.9	1013.0	62.4	253
1997	98	2203	12.96	53.3	1013.0	65.2	257
1997	98	2218	14.17	53.0	1013.0	66.4	265
1997	98	2233	12.78	52.7	1013.0	66.5	265
1997	98	2248	13.16	52.4	1013.0	66.4	265
1997	98	2303	12.64	51.9	1013.0	67.0	264
1997	98	2318	12.01	51.5	1013.0	66.4	258
1997	98	2333	12.67	51.3	1013.0	65.1	268
1997	98	2348	11.21	50.8	1013.0	66.3	265
1997	99	0003	10.98	50.5	1013.0	67.7	270
1997	99	0018	11.31	50.3	1013.0	67.3	280
1997	99	0033	8.57	50.5	1013.0	65.2	281
1997	99	0048	7.48	50.6	1013.0	63.6	285
1997	99	0103	5.85	50.0	1013.0	64.7	300
1997	99	0118	5.96	49.7	1013.0	65.3	282
1997	99	0133	4.92	48.9	1013.0	68.5	294
1997	99	0148	7.28	48.8	1013.0	70.1	278
1997	99	0203	6.66	48.6	1013.0	71.9	276
1997	99	0218	6.56	48.7	1013.0	71.5	276
1997	99	0233	6.09	48.5	1013.0	71.7	280
1997	99	0248	6.00	48.4	1013.0	72.0	271
1997	99	0303	6.92	48.3	1013.0	71.9	274
1997	99	0318	6.10	48.0	1013.0	72.9	277
1997	99	0333	7.52	48.1	1013.0	72.4	270
1997	99	0348	6.80	47.8	1013.0	72.1	267
1997	99	0403	5.59	47.5	1014.0	72.1	264

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	99	0418	5.11	47.1	1013.9	73.2	266
1997	99	0433	5.44	47.2	1013.7	71.7	268
1997	99	0448	6.47	47.2	1013.1	71.5	275
1997	99	0503	5.85	46.9	1013.0	72.0	276
1997	99	0518	5.00	46.4	1013.0	71.5	270
1997	99	0533	3.76	45.9	1013.0	71.2	274
1997	99	0548	3.50	45.7	1013.0	70.6	269
1997	99	0603	3.45	45.3	1013.0	71.1	275
1997	99	0618	4.09	45.0	1013.0	71.7	276
1997	99	0633	5.25	45.0	1013.7	71.8	278
1997	99	0648	3.04	44.1	1014.0	74.5	267
1997	99	0703	4.46	44.4	1014.0	76.3	270
1997	99	0718	5.23	45.2	1014.0	75.3	280
1997	99	0733	5.58	45.7	1014.0	73.3	279
1997	99	0748	4.23	46.7	1014.0	70.7	282
1997	99	0803	3.79	48.1	1014.0	66.8	301
1997	99	0818	4.10	49.2	1014.0	63.0	300
1997	99	0833	3.84	50.4	1014.0	59.4	313
1997	99	0848	4.25	51.7	1014.0	56.1	298
1997	99	0903	2.51	53.3	1014.0	53.2	323
1997	99	0918	3.70	54.1	1014.0	49.7	324
1997	99	0933	4.64	55.1	1014.0	45.0	259
1997	99	0948	5.52	55.3	1014.0	43.4	320
1997	99	1003	6.34	56.1	1014.0	43.1	281
1997	99	1018	5.87	57.5	1014.0	40.8	309
1997	99	1033	8.17	58.1	1013.9	38.1	258
1997	99	1048	7.03	59.1	1014.0	35.1	290
1997	99	1103	9.44	59.0	1013.5	35.1	215
1997	99	1118	7.20	60.1	1013.3	33.7	252
1997	99	1133	7.21	60.6	1013.0	33.1	300
1997	99	1148	7.38	61.8	1013.0	30.7	307
1997	99	1203	8.51	62.2	1013.0	28.9	306
1997	99	1218	6.74	63.3	1013.0	28.5	305
1997	99	1233	8.25	63.7	1012.5	27.2	283
1997	99	1248	7.35	64.4	1012.0	26.4	330
1997	99	1303	7.07	64.9	1012.0	26.1	267
1997	99	1318	3.69	65.8	1012.0	25.5	308
1997	99	1333	2.57	66.3	1012.0	24.6	291
1997	99	1348	3.82	66.0	1012.0	24.3	312
1997	99	1403	3.76	66.5	1012.0	23.0	302
1997	99	1418	3.01	66.9	1011.9	22.8	282
1997	99	1433	3.50	67.2	1011.1	22.2	317
1997	99	1448	2.07	67.9	1011.0	22.6	267
1997	99	1503	2.07	68.4	1011.0	21.9	331
1997	99	1518	1.66	68.7	1011.0	21.9	305
1997	99	1533	2.23	68.7	1011.0	22.4	305

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	99	1548	2.10	68.7	1011.0	23.2	308
1997	99	1603	2.51	69.2	1010.1	23.9	311
1997	99	1618	4.76	68.9	1010.0	24.3	271
1997	99	1633	5.34	69.1	1010.0	24.2	298
1997	99	1648	4.10	69.3	1010.0	24.3	314
1997	99	1703	4.31	69.5	1010.0	24.4	324
1997	99	1718	4.67	69.4	1010.0	24.2	293
1997	99	1733	3.15	69.8	1010.0	24.5	330
1997	99	1748	4.33	69.6	1010.0	24.4	313
1997	99	1803	7.20	69.0	1010.0	24.5	318
1997	99	1818	6.09	68.9	1010.0	24.9	315
1997	99	1833	6.64	68.4	1010.0	25.3	312
1997	99	1848	6.08	68.1	1010.0	25.6	308
1997	99	1903	7.49	67.7	1009.3	26.0	312
1997	99	1918	3.38	67.0	1009.0	27.1	307
1997	99	1933	3.97	66.0	1009.0	27.8	309
1997	99	1948	2.92	65.0	1009.0	29.2	310
1997	99	2003	1.44	64.3	1009.0	29.6	295
1997	99	2018	8.23	61.0	1009.9	49.9	268
1997	99	2033	7.57	59.7	1010.0	56.3	274
1997	99	2048	7.26	58.5	1010.0	59.1	270
1997	99	2103	8.07	57.8	1010.0	61.2	275
1997	99	2118	6.94	57.0	1010.0	64.1	277
1997	99	2133	6.40	56.6	1010.1	65.4	276
1997	99	2148	5.67	56.0	1010.7	67.7	277
1997	99	2203	5.82	55.5	1011.0	69.6	272
1997	99	2218	6.52	55.5	1011.0	70.6	277
1997	99	2233	6.52	55.3	1011.0	71.7	279
1997	99	2248	6.04	55.1	1011.0	72.5	277
1997	99	2303	5.22	54.7	1011.0	73.3	277
1997	99	2318	3.88	54.2	1011.0	74.3	282
1997	99	2333	1.88	53.6	1011.0	75.4	322
1997	99	2348	0.27	52.4	1011.0	76.7	169
1997	100	0003	0.00	50.4	1010.9	80.3	50
1997	100	0018	0.00	49.6	1011.0	80.6	339
1997	100	0033	0.00	49.6	1011.0	81.7	90
1997	100	0048	0.00	49.0	1011.0	82.1	199
1997	100	0103	0.00	49.3	1011.0	80.6	299
1997	100	0118	0.02	50.6	1011.0	76.0	287
1997	100	0133	0.00	50.5	1011.0	73.9	317
1997	100	0148	0.00	50.4	1011.0	73.3	299
1997	100	0203	1.04	51.2	1010.5	72.2	309
1997	100	0218	2.58	52.3	1010.0	70.6	294
1997	100	0233	0.49	51.6	1010.0	71.6	294
1997	100	0248	0.35	50.7	1010.0	74.0	287
1997	100	0303	0.22	50.2	1010.0	75.1	297

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	100	0318	0.92	50.2	1010.0	77.1	286
1997	100	0333	0.43	49.8	1010.0	78.6	295
1997	100	0348	0.00	48.9	1010.0	79.7	161
1997	100	0403	0.00	47.5	1010.0	83.1	25
1997	100	0418	0.02	46.3	1010.0	83.4	253
1997	100	0433	0.00	46.1	1010.0	82.8	319
1997	100	0448	0.09	46.4	1010.0	80.9	295
1997	100	0503	1.85	46.9	1010.0	74.9	318
1997	100	0518	2.83	47.7	1010.0	68.4	322
1997	100	0533	2.97	47.6	1010.0	67.2	288
1997	100	0548	1.74	47.8	1010.0	66.3	306
1997	100	0603	3.60	47.8	1010.0	66.4	285
1997	100	0618	2.33	47.4	1010.0	67.7	297
1997	100	0633	2.35	47.9	1010.7	66.1	294
1997	100	0648	2.59	48.0	1011.0	65.6	336
1997	100	0703	2.48	48.1	1011.0	66.8	278
1997	100	0718	1.68	48.5	1011.0	66.9	270
1997	100	0733	0.14	50.0	1011.0	65.2	331
1997	100	0748	0.74	50.9	1011.0	63.1	313
1997	100	0803	1.94	52.0	1011.5	61.6	325
1997	100	0818	2.75	53.0	1012.0	59.6	298
1997	100	0833	3.16	53.8	1012.0	58.5	189
1997	100	0848	2.47	55.2	1012.0	56.0	248
1997	100	0903	6.08	55.1	1012.0	53.2	186
1997	100	0918	4.11	56.0	1012.0	53.6	230
1997	100	0933	3.07	57.1	1012.0	53.1	192
1997	100	0948	3.34	58.1	1012.0	51.3	205
1997	100	1003	2.25	59.6	1012.0	48.4	293
1997	100	1018	2.27	60.6	1012.0	46.7	280
1997	100	1033	2.51	61.8	1012.0	44.3	227
1997	100	1048	3.40	62.0	1012.0	42.9	267
1997	100	1103	1.07	62.9	1012.0	42.2	288
1997	100	1118	2.22	63.9	1012.0	40.5	243
1997	100	1133	2.29	64.3	1012.0	39.9	319
1997	100	1148	1.60	65.5	1012.0	38.7	266
1997	100	1203	1.06	65.8	1012.0	37.7	267
1997	100	1218	1.13	67.1	1012.0	37.1	260
1997	100	1233	1.53	67.7	1011.7	35.8	249
1997	100	1248	1.46	68.6	1011.0	34.6	303
1997	100	1303	1.27	69.2	1011.0	33.8	271
1997	100	1318	0.56	70.3	1011.0	32.5	321
1997	100	1333	0.73	70.9	1011.0	30.7	309
1997	100	1348	0.01	71.4	1010.9	29.2	302
1997	100	1403	0.00	71.8	1010.1	28.9	320
1997	100	1418	0.04	72.4	1010.0	27.4	328
1997	100	1433	0.03	72.5	1010.0	26.1	286

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	100	1448	0.02	73.1	1010.0	26.1	276
1997	100	1503	1.30	72.5	1010.0	23.5	278
1997	100	1518	0.27	72.9	1010.0	22.8	302
1997	100	1533	0.16	72.8	1009.5	22.3	272
1997	100	1548	0.21	73.2	1009.0	23.6	302
1997	100	1603	0.39	73.1	1009.0	23.1	308
1997	100	1618	1.66	73.2	1009.0	22.5	285
1997	100	1633	0.62	73.5	1009.0	22.0	327
1997	100	1648	1.30	73.5	1008.9	20.7	259
1997	100	1703	1.19	73.5	1008.3	21.5	323
1997	100	1718	4.15	72.9	1008.0	19.2	307
1997	100	1733	2.74	73.2	1008.0	19.4	319
1997	100	1748	1.55	73.0	1008.0	21.9	314
1997	100	1803	3.75	72.1	1008.0	26.3	280
1997	100	1818	4.48	71.4	1008.0	28.3	279
1997	100	1833	8.19	70.0	1008.0	33.1	282
1997	100	1848	10.08	68.9	1008.0	36.9	267
1997	100	1903	7.61	68.1	1008.0	39.9	272
1997	100	1918	10.26	66.8	1008.0	40.6	269
1997	100	1933	6.57	65.3	1008.1	44.1	278
1997	100	1948	6.47	64.3	1009.0	43.5	275
1997	100	2003	6.61	63.4	1009.0	44.6	272
1997	100	2018	7.25	62.7	1009.0	46.8	274
1997	100	2033	6.76	62.1	1009.0	46.9	272
1997	100	2048	7.87	61.7	1009.0	45.3	265
1997	100	2103	6.57	60.9	1009.0	46.7	264
1997	100	2118	5.15	60.2	1009.0	49.9	265
1997	100	2133	5.28	59.7	1009.0	51.7	270
1997	100	2148	4.24	58.7	1009.0	54.1	275
1997	100	2203	4.32	57.9	1010.0	55.3	253
1997	100	2218	2.63	56.9	1010.0	58.1	267
1997	100	2233	5.85	57.3	1010.0	58.7	272
1997	100	2248	6.45	57.3	1010.0	60.1	270
1997	100	2303	5.18	57.0	1010.0	61.2	272
1997	100	2318	4.52	56.3	1010.0	63.1	278
1997	100	2333	5.38	56.0	1010.0	64.3	274
1997	100	2348	4.17	55.8	1010.0	63.9	284
1997	101	0003	3.96	55.9	1010.0	61.6	292
1997	101	0018	3.29	56.0	1010.0	59.0	282
1997	101	0033	1.20	54.9	1010.0	62.4	286
1997	101	0048	0.00	53.5	1010.0	65.6	155
1997	101	0103	0.12	53.1	1010.0	65.2	282
1997	101	0118	0.61	52.6	1010.0	65.4	299
1997	101	0133	0.00	51.3	1010.1	66.6	328
1997	101	0148	0.09	50.5	1011.0	66.6	324
1997	101	0203	0.64	50.0	1011.0	63.2	332

ENDOSULFAN APPLICATION METEOROLOGICAL DATA (15 min. averages)

Year	Julian Date	Time	Wind Speed (mph)	Temp. (F)	Barometric Pressure (hPa)	Relative Humidity	Wind Direction (degrees)
1997	101	0218	1.19	49.0	1011.0	71.8	324
1997	101	0233	3.09	48.2	1011.0	79.0	68
1997	101	0248	3.82	46.9	1011.0	82.5	45
1997	101	0303	1.08	46.6	1011.0	82.8	190
1997	101	0318	0.00	46.3	1011.0	81.1	283
1997	101	0333	0.00	46.6	1011.0	79.7	240
1997	101	0348	0.35	45.4	1011.0	80.0	262
1997	101	0403	0.00	44.9	1011.0	81.1	282
1997	101	0418	0.00	45.0	1011.0	79.7	275
1997	101	0433	0.01	45.5	1011.0	76.6	294
1997	101	0448	0.03	45.6	1011.0	73.6	325
1997	101	0503	0.27	46.0	1011.0	68.8	322
1997	101	0518	0.26	45.7	1011.1	67.5	333
1997	101	0533	0.25	45.4	1011.5	65.3	338
1997	101	0548	0.61	45.8	1011.9	62.4	332
1997	101	0603	1.19	46.6	1012.0	59.7	328
1997	101	0618	3.64	47.3	1012.0	58.5	200
1997	101	0633	3.07	47.0	1012.0	59.7	297
1997	101	0648	2.60	46.7	1012.0	61.0	227
1997	101	0703	2.95	46.8	1012.0	62.2	98
1997	101	0718	1.96	47.3	1012.2	62.9	170
1997	101	0733	0.09	49.0	1013.0	62.0	147
1997	101	0748	0.65	50.6	1013.0	61.0	212
1997	101	0803	4.54	50.4	1013.0	59.0	151
1997	101	0818	6.28	50.7	1013.0	58.2	107